ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

INVESTIGATION OF DIFFERENT COMPATIBILIZERS EFFECTS ON THE PROPERTIES OF POLYOLEFIN NANOCOMPOSITES

M.Sc. THESIS

Mert Emre ÖZTOKSOY

Department of Polymer Scinence and Technology

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

POLİOLEFİN NANOKOMPOZİTLERİN ÖZELLİKLERİNE FARKLI UYUMLAŞTIRICILARIN ETKİSİNİN ARAŞTIRILMASI

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MAYIS 2014

Mert Emre Öztoksoy, a **M.Sc.** student of ITU **GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY** student ID **515111026**, successfully defended the **thesis** entitled "**INVESTIGATION OF DIFFERENT COMPATIBILIZERS EFFECTS ON THE PROPERTIES OF POLYOLEFIN NANOCOMPOSITES**", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my family,

FOREWORD

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May 2014

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ABBREVIATIONS

PE	**:** Polyethylene
PP	**:** Polypropylene
PO	**:** Polyolefins
PCN	**:** Polymer Clay Nanocomposites
PNC	**:** Polymer nanocomposite
PLS	**:** Polymer layered silicate
PE-g-MA	**:** Polyethylene grafted maleic anhydride
PE-co-MA	**:** Polyethylene copolymer maleic anhydride
PP-g-MA	**:** Polypropylene grafted maleic anhydride
MMT	**:** Montnorillonite
XRD	**:** X-ray Diffraction
DSC	**:** Differential Scanning Calorimeter
MFI	**:** Melt Flow Index
MFR	**:** Melt Flow Rate
GWT	**:** Glow wire test

LIST OF SYMBOLS

$\mathbf{T_c}$	**:** Crystallization temperature
$\mathbf{T_m}$	**:** Melting temperature
$\mathbf{\Delta H_c}$	**:** Crystallization entalphy
$\mathbf{\Delta H_m}$	**:** Entalphy of fusion
%Xc	**:** % crystalinity
θ	**:** Direction of the beam
λ	**:** Wavelength

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INVESTIGATION OF DIFFERENT COMPATIBILIZERS EFFECTS ON THE PROPERTIES OF POLYOLEFIN NANOCOMPOSITES

SUMMARY

Polyolefins are the most important polymeric materials which are processed usually by extrusion. Polyethylene is widely used as polyolefin in the industry.

Nanocomposites are a combination of two or more phases containing different compositions, where at least one of the phases is within the nanoscale range. Polyolefins/ clay nanocomposites (PNC) are prepared as more difficult than any polymer because of containing polar groups in its backbone. Homogeneous dispersion of polar clay can not be realized due to lack of polyolefins miscibility with organically-modified clay (organoclay). A strong interaction between a non-polar polymer (e.g. PE and PP) and polar organoclay may be achieved with addition of a compatibilizer. The convenient way of preparing a compatibilizer is functionalization of the original polyolefins.

In this study, the polyolefin nanocomposites having different compositions of polyethylene or polypropylene matrix, modified clay and different compatibilizers were prepared by melt compounding method by using twin screw extruder mixing temperature between a of 170^{o}C-210^{o}C and at 350 rpm screw speed, and then using injection molding for analysis. The effects of organoclay type (I-44 clay and I-30 clay), type and percent of compatibilizers; on the morphology, thermal, mechanical and flow properties of nanocomposites were investigated. In order to prepare of PE/clay nanocomposite, PE-co-MA (polyethylene copolymer maleic anhydride) and PE-g-MA (polyethylene grafted maleic anhydride) were used as compatibilizer. For the preparation of PP/clay nanocomposite of PE-co-MA and PP-g-MA (polypropylene grafted maleic anhydride) were used as compatibilizers. In the

production of PE/clay nanocomposites, the 5wt% clay (I-30 and I-44) was used with the two different compatibilizers which are PE-co-MA or PE-g-MA. For the production the PE-co-MA, the different amount of compatibilizers (5, 10 and 15wt%) were used in order to determine the optimum amount of compatibilizer. Also the PE-g-MA was used only the amount of 15wt% in order to obtain highest mechanical properties which supported by several studies in the literature. In addition, PP/clay nanocomposites were prepared with the clay of I-44 in order to make a comparison. These nanocomposites have prepared with the amount of 15wt% PE-co-MA and 15wt% PP-g-MA and the amount of 5wt% PE-co-MA.

Afterwards, in order to obtain the mechanical properties of nanocomposites, samples were subjected to the some tests such as tensile test, impact test and hardness test. Tensile strength, tensile modulus, yield strength, yield strain, strain at break were examined in tensile test. Also, the effect of compatibilizer on mechanical properties are compared by using tensile test results. PE/I-30 clay nanocomposites are increased the modulus of nanocomposites. Izod impact test was used to obtain the strength of polyolefin nanocomposites whereas the hardness test was used to compare the mechanical properties with the other tests.

The XRD, DSC and ash testing were used in order to characterize morphological and thermal properties. The XRD measurements of polyethylene nanocomposites containing different compatibilizers (15wt% PE-co-MA and PE-g-MA) were measured to investigate the effect of mixing between clay and polyolefin on the properties of these nanocomposites. The partial exfoliation was observed for these nanocomposites. Also, DSC analyses were done in order to determine the thermal behavior of all samples and the effects of modified clays and compatibilizers on thermal behavior of nanocomposites. Melting temperatures (Tm), crystallization temperatures (Tg), the entalphy of melting (ΔHm), the enthalpy of crystallization (ΔHc) and % crystalinity values of the compounds were found from DSC diagrams. The percent crystallinity values were calculated as the ratio of the heat of fusion of the sample (ΔHm), divided by the weight fraction of the polymer in the nanocomposite and the heat of fusion of the pure crystalline form of the polymer. In ash testing, the inorganic content of clays are measured.

The flow properties of molten polymer are described as melt flow index (MFI) or melt flow rate (MFR). The melt flow index test was used to specify of average

molecular mass of nanocomposites and the flow behavior of molten polymer which is an important factor that affects the workability of polymers.

The glow wire test at 650˚C was done to compare the ability of materials to extinguish flames and their ability. All the nanocomposites passed the test successfully.

POLİOLEFİN NANOKOMPOZİTLERİN ÖZELLİKLERİNE FARKLI UYUMLAŞTIRICILARIN ETKİSİNİN ARAŞTIRILMASI

ÖZET

Poliolefinler, polimerik malzemeler içerisinde önemli bir yere sahiptirler. Polimerlerin işlenme kolaylığı, mekanik davranışları, esnek yapıları ve düşük yoğunluğa sahip olmaları ve ucuz olmaları önemli avantajlarıdır. Günümüzde ticari olarak en çok kullanılan poliolefinler, polietilen ve polipropilendir. Endüstride genel olarak eriyik harmanlama yöntemi ile kullanılır ve en çok kullanılan eriyik harmanlama yöntemi ekstrüzyondur. Poliolefinlerin kullanılması için bazı mekanik, termal ve morfolojik özelliklerinin iyileştirilmesi gerekmektedir. Bu özellikler genellikle organik veya inorganik katkılarla geliştirilir. Bu katkılı polimerik matrisler nano boyuttaki inorganik katkılarla karıştırılmalarına nanokompozit denir.

Nanokompozitler en az biri nano boyutta olan iki farklı fazın birleşiminden oluşurlar. İstenen özellikte polimer matrisli nanokompozit numune elde edebilmenin ön koşulu taneciklerin matris içerisinde düzenli dağılmış olmalarıdır. Poliolefin/kil nanokompozitlerin yapılarında bulunan polar gruplardan dolayı üretimi diğer herhangi bir polimerin üretiminden daha zordur. Poliolefinler, kil ile karışamadığı için bu kompozit oluşturulurken homojen bir dağılım gerçekleşmemektedir. Kil modifiye edilerek ve uyumlaştırıcı eklenerek, polietilen ve polipropilen gibi apolar polimer ile kil arasında güçlü bir etkileşim gerçekleştirilir. Uyumlaştırıcı oluşturmanın en uygun yolu orijinal poliolefinlerin fonksiyonlanmasıdır. En çok kullanılan uyumlaştırıcılar maleik fonksiyonlu poliolefinlerdir. Bunlardan en geniş kapsamlı olarak kullanılanlar polietilen aşılanmış maleik anhidrit ve polipropilen aşılanmış maleik anhidrittir. Killer ise amonyum tuzları ile modifiye edilebilirler.

Bu çalışmada, poliolefin nanokompozitler farklı bileşime sahip polietilen veya polipropilen matris, modifiye kil ve farklı uyumlaştırıcılar kullanılarak

hazırlanmıştır. Kompozit malzemelerin üretimi çift vidalı ekstruder ile 170^{o}C - 200^{o}C karışma sıcaklığı aralığında 350 rpm vida hızında eriterek karıştırma metodu ile yapılmıştır. Kullanılan modifiye killerin, farklı uyumlaştırıcıların, bileşenlerin karışım oranlarının kompozit malzemeye olan etkileri morfolojik, termal ve mekanik testlerle araştırıldı. PE/kil nanokompozit malzemeleri oluşturulurken PE-co-MA (maleik anhidrit ile kopolimerleştirilmiş polietilen) veya PE-g-MA (maleik anhidrit aşılanmış polietilen) uyumlaştırıcıları ve PP/kil nanokompozitleri hazırlanırken de PE-co-MA veya PP-g-MA (maleik anhidrit aşılanmış maleik anhidrit) uyumlaştırıcıları kullanıldı. I-44 ve I-30 kil çeşitleri de modifiye kil olarak nanokompozit malzemeleri üretiminde kullanılmıştır.

Polietilen/kil nanokompozitler, %5 ağırlıkça organokile (I-44 ve I-30), iki çeşit uyumlaştırıcının (PE-co-MA/PE-g-MA) farklı oranlarda eklenmesiyle üretildi. PE-co-MA uyumlaştırıcı %5, %10 ve %15 oranında kullanılırken, PE-g-MA uyumlaştırıcısı %15 oranında kullanıldı. PE/kil nanokompozitler ile karşılaştırma amacı için üretilen PP/kil nanokompozitleri üretiminde %5 oranında sadece I-44 kili kullanıldı. PP/kil nanokompozitlerinde %15 oranında PP-g-MA ve %5 ve %15 oranında PE-co-MA uyumlaştırıcıları kullanıldı.

Nanokompozitlerin üretiminden sonra malzemelerin mekanik özellikleri belirlemek için çekme testi, darbe testi ve sertlik testleri yapıldı. Çekme testinde çekme kuvveti, çekme modulü, akma kuvveti gibi malzemenin mekanik özellikleri belirlendi. Ayrıca, kil ve poliolefin arasındaki etkileşimi arttırmak için kullanılan uyumlaştırıcıların kompozitin mekanik özelliklerine etkisi de incelendi. Çıkan sonuçlarda modül değerinde bir artış gözlendi. Izot darbe testi poliolfin/kil nanokompozitlerinin dayanımını belirlemek için yapıldı. Ayrıca malzemenin mekanik özelliklerinin desteklenmesi için sertlik testi de malzemelere uygulandı.

Poliolefin/kil nanokompozit malzemelerin morfolojik ve termal özelliklerini belirlemek için XRD, DSC ve kül testleri uygulandı. XRD ölçümü polietilen/kil nanokompozitlerinde literatürlerde en iyi uyum %15 uyumlaştırıcı ile %5 kil karışımlarında görüldüğü için %15 PE-co-MA ve %15 PE-g-MA kullanılarak yapıldı. XRD analizinde kil ve polietilen ile hazırlanan nanokompozitlere uyumlaştırıcıların etkisi araştırıldı. Bulunan sonuçlarda tabakalar arası açılmanın olduğu ve tabakaların kısmi dağıtılmış olduğu gözlendi.

Ayrıca, DSC analizi bütün örneklere uygulandı ve bu analizde modifiye killerin ve uyumlaştırıcıların nanokompozitlerin termal özellikleri üzerinde etkisi de araştırıldı. DSC spektrumlarından erime sıcaklığı (Tm), kristalizasyon sıcaklığı (Tc), erime entalpisi (ΔHm), kristalizasyon entalpisi (ΔHc) ve % kristallizasyon değerleri bulundu. Kül testi de kildeki inorganik içeriğinin analizi için poliolefin/kil nanokompozit malzemelere uygulandı.

Eriyik polimerin akma özellikleri erime akış indeksi (MFI) ile belirlenerek poliolefin/kil nanokompozitlerinde nanokatkının polimerin işlenebilirliğine etkisi incelendi.

Ayrıca, kızgın tel deneyi ile de nanokompozit malzemelerin alevlenme özellikleri incelendi. Hazırlanan bütün nanokompozitler 650˚C deki kızgın tel deneyinden başarı ile geçmiştir.

1. INTRODUCTION

Polyolefins (PO) are one of the fastest growing comsumed commercial thermoplastic materials because of its low cost and desirable properties such as high strength, good barrier properties, light weight, water resistance, chemical resistance and higher stability.

Increasing demand for using them forced the scientists to improve their properties. Therefore, in recent years, inorganic fillers are often added to polyolefins to form composites or nanocomposites in which the filler serves to enhance the mechanical properties [1].

The clay component here largely serves as a filler or extender in order to reduce the cost of the final product although rigidity and strength are often improved. In 'nanocomposites', on the other hand, the incorporated clay particles have at least one dimension in the nanometre range (<100 nm), providing an extensive surface area for interaction with the polymer phase. More valuable, the more or less uniform dispersion of nanosize clay particles in the polymer matrix leads to significant improvements in mechanical and thermal properties with only a minor increase in cost [2].

Clay have some advantages such as large interlayer surface area, high cation exchange capacity, expansibility in water and propensity for intercalating organicmolecules. The clay also are naturally hydrophilic due to the presence of hydrated inorganic counterions in the interlayer space. These minerals are therefore immiscible with many non-ionic organic polymers since the latter are essentially hydrophobic, especially those that are non-polar such as polyethylene and polypropylene. One way of overcoming the chemical incompatibility between mineral and polymer is to attach polar functional groups to either the mineral surface. The main type of nanoclay that has attracted most attention in polymer nanocomposites is based on the natural mineral 2:1 double layered silicate clays, particularly the plate-like montmorillonite (MMT) [3].

Nanocomposites are a class of filled polymers in which inorganic fillers such as clay at the nanometre scale are dispersed in a polymer matrix.

PE/clay and PP/clay nanocomposites are usually prepared by melt-mixing process, and the other processing techniques are in situ polymerization and solution dispersion process. The compatibilizers must be used in mixing polyolefins and clays even if the clays are organoclays. These compatibilizers are required due to the huge polarity difference between the polyolefin matrix and the clay. Compatibilizers are generally used in the form of maleic anhydride derivatives such as PP grafted maleic anhydride (PP-g-MA), PE grafted maleic anhydride (PE-g-MA). They allows wetting of the clay surface by hydrogen-bond interactions between the anhydride functions (acid functions when hydrolyzed) and the oxygen atoms at the surface of the clay layers. Even when using organoclay and compatibilizers, PO/Clay reinforced polymer nanocomposites (PNCs) have attracted great interest in the recent past due to the low nanofiller concentration typically required (1–5% compared to 30–40% for conventional fillers and fibres) and the abundance and low cost of the nanoclay fillers combined with significant benefits in terms of the performance properties of the resultant nanocomposites, and principally thermal properties, fire retardancy and barrier properties. [3].

2. THEORETICAL PART

2.1 Polyolefins

Polyolefins are synthetic of olefic monomers. They are the largest polymer family by volume of production and consumption. Several million metric tons of polyolefins are produced and consumed worlwide each year, and as such they are regarded as commodity polymers. Polyolefins have enjoyed great success due to many application opportunities, relatively low cost, and wide range of properties. Polyolefins are recyclable and significant improvement in properties is available via blending and composites technologies. To improve the properties of the pure polymers and hence to expand the horizon of applications, the polymers are incorporated with inorganic fillers which leads to the improvement in a number of mechanical, thermal, load bearing properties [4].

Polyolefins may be classified based on their monomer unit and chain structures as ethylene-based polyolefins, polypropylene-based polyolefins, higher polyolefins and polyolefins elastomer [5]. Polyethylene and polypropylene represent a versatile class of materials with a combination of good properties and low cost [4].

2.1.1 Structure of polyethylenes

Polyethylene is classified into several different categories based mostly on its density and branching .The mechanical properties of PE depend significantly on variables such as the extent and the type of branching, the percent crystalinity, and the molecular weight.

Polyethylene (PE) was discovered in 1933 by Reginald Gibson and Eric Fawcett at the British industrial giant, Imperial Chemical Industries. Although it is more than 70 years since it was first produced, it is still a very promising material. This widely used plastic is a polymer ethylene, $CH_2=CH_2$, having the formula $(-CH_2CH_2-)_n$. It is produced at high pressures and temperatures in the presence of any one of several catalysts, depending on the desired properties of end-use product. Other structures

(leading to long and short branches) may be present, depending on the procedure used in synthesis. PE is the largest volume polymer consumed in the world. It is a versatile material that offers high performance compared to other polymers and alternative materials such as glass, metal or paper. Polyethylene (PE) grades are mainly classified according to their density.

2.1.1.1 Low-density polyethylene (LDPE)

LDPE is a semi-rigid, semi transparent material, and was the first of the polyethylenes to be developed. It is primarily used at 'normal' operating temperatures. It is qualities include toughness, flexibility, resistance to chemicals and weather, and low water absorption. It is easily processed by most methods and has a low cost. it is also resistant to organic solvents at room temperature. its use is not advisable in situations where extreme temperature are found. LDPE has a fairly low working temperature so it is easy to extruded materials. Today, it has almost fully been replaced by LLDPE. The main market for LDPE is in high-clarity products ,which includes produce bags, bakery film, and textile and paper overwrap.

Overall film use is declining by 0.4% per year. Aside from extrusion coatings and adhesives and sealants, LDPE's other application segments are declining 2-3% annually, largely as a result of displacement by LLDPE .

Figure 2.1 : Low density polyethylene

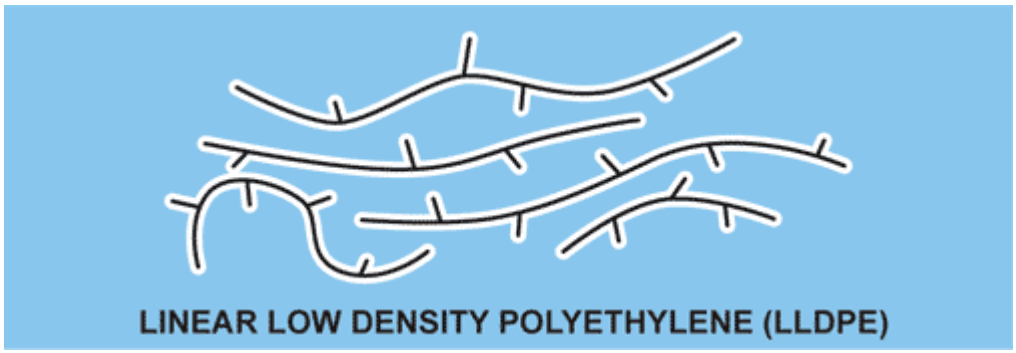

Figure 2.2 : Linear low density polyethylene

2.1.1.2 High-density polyethylene (HDPE)

HDPE is more rigid and harder than lower density materials with a molecular weight below 300,000 g/mol. It also has a high tensile strength, four times that of LDPE, and has high compressive strength. HDPE has exceptional impact strength, being one of the best impact-resistant thermoplastics available, and has excellent machinability and self-lubricating characteristics. Its properties are maintained even at extremely low temperatures. HDPE has stress cracking resistance and very good chemical resistance to corrosives. HDPE is stronger and stiffer than LDPE but its impact strength is not as good at low temperatures. Extrusion grades are frequently used in wire coating, pipes and cable insulation. HDPE does have certain disadvantages. It is susceptible to stress cracking, has lower stiffness compared to polypropylene (PP), high mould shrinkage, and poor UV resistance.[6]

Figure 2.3 : High density polyethylene

2.1.2 Polypropylene

Crystalline polypropylene was discovered in the early 1950s and it is commercially produced in Italy on 1957, Germany, and the USA. Since that modest beginning,

polypropylene has become among the most important synthetic polymers produced by humankind ranking second only polyethylene.

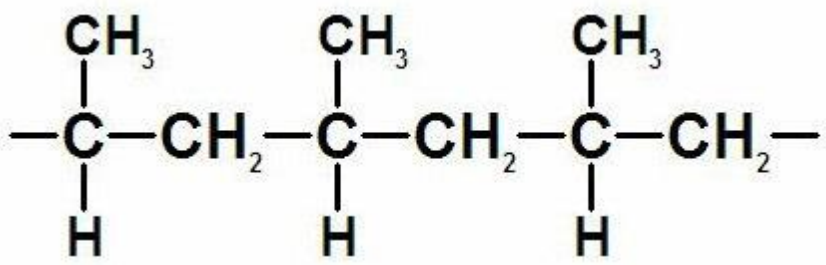

Figure 2.4 : Molecular structure of polypropylene chain.

Polypropylene is extensively used in the world owing to the widespread availability, low cost monomer, low manufacturing cost and desirable properties. Furthermore, workability in variety of different processing equipment, ranging from injection molding, calendaring and blown film equipment due to its proper melt rheology and thermal behavior supports the industrial demand, and approximately 55 million metric tons of polypropylene were manufactured globally in 2011 [7-9].

2.2 Overview of Clay

Over the last decade, various types of nanofillers have been used for the preparation of composites with almost all types of polymer matrices although polymer nanocomposites based on clays attract great interest in today's materials research because it is possible to achieve impressive property enhancements when compared with neat polymers or conventional filler-filled composites [10]. These improvements may include high moduli, increased strength and heat resistance, decreased gas permeability and flammability, and the increased degradabilityof biodegradable polymers [10-11]. Additionally,there has been considerable interest in theory and simulations addressing the preparation and properties of these materials, which are also considered to be unique model systems, to study the structure and dynamics of polymer chains in confined environments [12-16]. Moreover, clays are naturally abundant, economical, and more important, benign to the environment [17].

Among all minerals, silicates constitute the largest and most interesting and complex class of minerals available on earth. The basic chemical unit of silicates is SiO_4, a

tetrahedron-shaped anionic group with a charge of -4. The complex structures that these silica tetrahedrons form are truly amazing. They can form single units (known as nesosilicates), double units (known as sorosilicates), chains (known as inosilicates), sheets (known as phyllosilicates), rings (known as cyclosilicates), and framework structures (known as tectosilicates) [18]. The different ways that silicate tetrahedrons combine is what makes the silicate ckass the largest, most interesting, and most complex class of minerals.

Clays are found mixed or associated with other minerals and amorphous materials. The identification of clays in a raw clay or soil always requiresa purification step. This is because the presence of carbonates, iron oxides, organic minerals, and the like interferes with the identification procedure. Purification is very important for the application of clays in the manufacture of polymer nanocomposites [19].

The most typically used clays for the preparation of polymer nanocomposites belong to the family of phyllosilicates, that is, layered or sheetlike structures more commonly referred to as layered silicates [20]. Layered silicates have two types of structures:tetrahedrally substituted and octahedrally substituted. In the case of tetrahedrally substituted layered silicates, the negative charge is located on the surface of the silicate layers,and hence,the polymer matrices can react-interact more readily with those that with octahedrally substituted material. Generally, clay minerals are divided into three major groups:

Smectite group: This group consist of several layared silicate minerals, the most important of which are vermiculate, saponite, hectorite, montmorillonite, talc, sauconite, and nontronite. The general formula of these members is $(Ca,Na,H)(Al,Mg,Fe,Zn)_2(Si,Al)_4O_{10}(OH)_2$-$xH_2O$, where x represents the variable amount of the kaolinite group are replaced by a similar layer, known as oxide brucite, $Mg_2(OH)_4$. The structure of this composed of silicate layers with a brucite layer sandwiched in between, and water molecules are present between the sandwich layers .

Table 2.1 : Properties of MMT

Surface Area	Modulus	Density	Inter Layer Thickness
750-800 m2/g	178-220 GPa	2.385 g/ml	1.45 nm

Montmorillonite crystal structure consists of stacked layers made of two silica tetrahedrons fused to an edge-shared octahedral sheet of alumina or magnesium hydroxide [12].

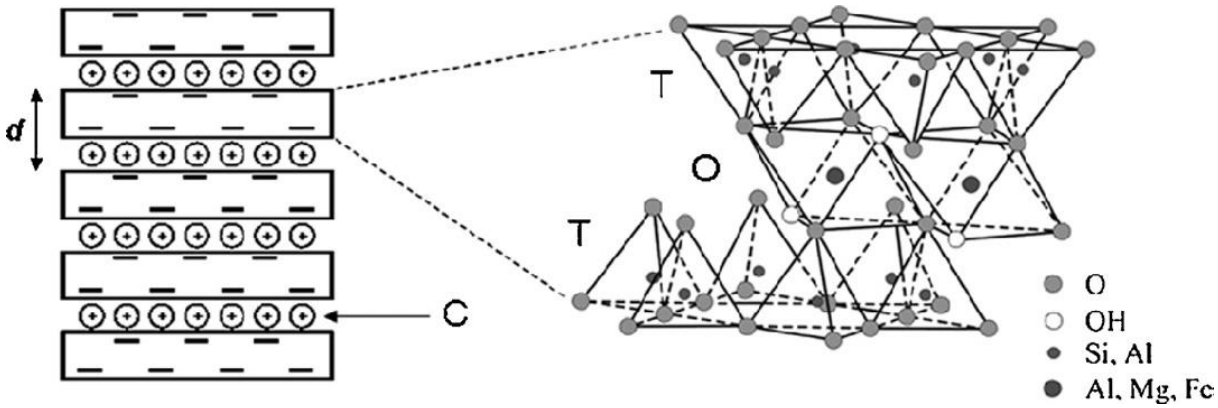

Figure 2.5 : Crystal structure of montmorillonite

One important consequence of the charged nature of the clays is that they are generally highly hydrophilic species and therefore naturally incompatible with a wide range of polymer types. In clays the space between the closely packed sheets are on the order of ~1 nm. Thus there is a large entropic barrier associated with the molten polymer diffusing into the gap and hence, intercalation into the layered clay is hindered. Accordingly, the clay must be treated before it can be used to make a nanocomposite otherwise it will be dispersed as microcomposite.

2.3 Polymer-Clay Nanocomposites

2.3.1 Structure of polymer-clay nanocomposites

Conditional upon the interactions between the clay and the polymer matrix, two main idealized types of polymer-clay morphologies can be obtained, namely, intercalated and exfoliated. In the intercalated nanocomposites, a single (and sometimes more than one) extended polymer chains is intercalated between the silicate layers, resulting in a well-ordered multiplayer morphology built up with alternating polymeric and silicate layers. In exfoliated nanocomposites, the silicate layers of MMT are completely separated into individual nanometer thick (about 1nm) layers and uniformly dispersed in the continuous polymer matrix [21].

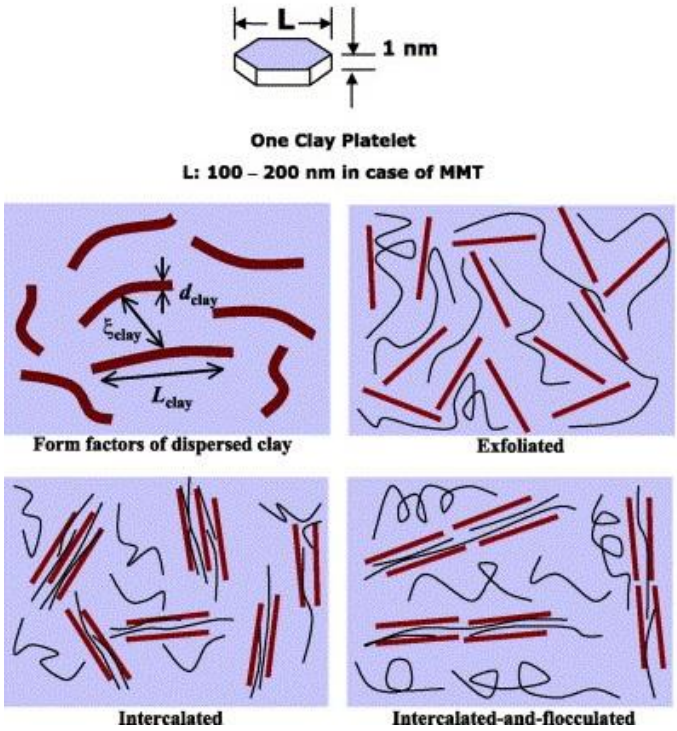

Figure 2.6 : Interactions between the clay and the polymer matrix

There is also a structure which is called flocculated similar with intercalated nanocomposites, however silicate layers are sometimes flocculated due to hydroxlated edge-edge interaction of the silicate layers, phase separation might be observed in this structure [10], because of this it can not be accepted as a nanocomosite.

Preliminary studies on nanocomposites have shown that largest improvements in mechanical and physical properties are obtained in exfoliated morphology. Because of this it is important to obtain exfoliated structure when preparing PCN.

2.3.2 Preparation of polymer-clay nanocomposites

Any physical mixture of a polymer and layerde silicate does not form a nanocomposite. This situation is analogous to polymer blends, and in most cases separation into discrete phases commonly takes place. In immiscible system, which typically correspond to the more conventionally filled polymers, the poor physical interaction between the organic and inorganic components leads to poor mechanical and thermal properties. In contrast, the strong interactions between the polymer and the layered silicate in PLS nanocomposites lead to the organic and inorganic phases

being disperse at the nanometer level. As a result nanocomposites exhibit unique properties not shared by their micro counterparts or conventionally filled polymers. Pristine layered silicates usual contain hydrated Na^+ or K^+ ions. Certainly, in this pristine state layered silicates are only compatible with hydrophilic polymers, such as polyethylene oxide (PEO), polyvinyl alcohol (PVA) etc. To render layered silicates compatible with other polymer matrices, one must convert the normally hydrophilic silicate surface to organophilic, which makes the intercalation of many engineering polymers possible. In general, this can be done by ion-exchange reactions with cationic surfactants including primary, secondary, tertiary, and quaternary alkyl ammonium or alkyl phosphonium cations. The role of alkyl ammonium or alkyl phosphonium cations in the organosilicates is to lower the surface energy of the inorganic host and to improve the wetting characteristics with the polymer matrix, and results in a larger interlayer spacing. One can evaluate that about 100 alkylammonium salt molecules are localised near the individual silicate layers (~$8x10^{-15}m^2$) and active surface area (~$800m^2/g$) [10].

Also, alkylammonium or alkyl phosphonium cations could provide functional groups that can react with the polymer matrix or in some cases initiate the polymerization of monomers to improve the strength of the interface between the inorganic and polymer matrix [22-23].

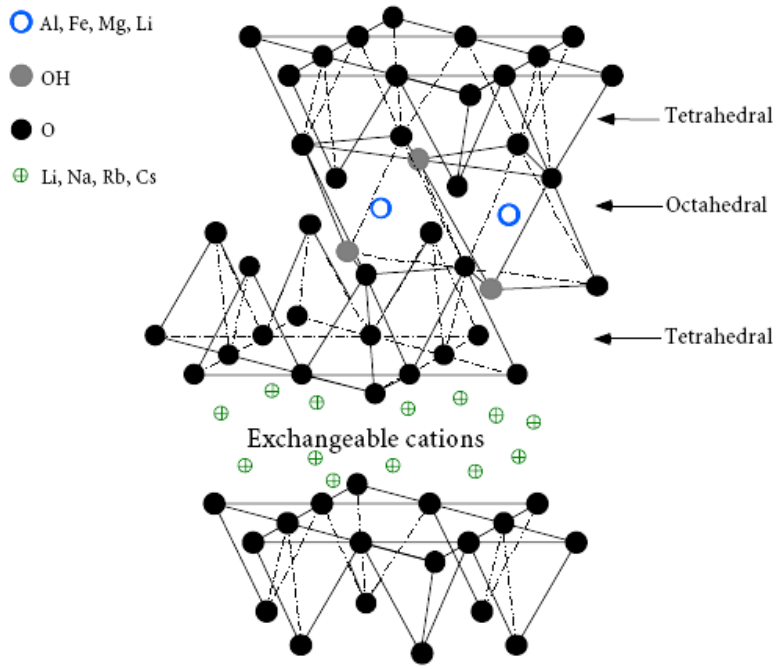

Figure 2.7 : Structure of 2:1 phyllosilicates

Intercalation of polymers in layared silicates, has proven or pre-polymer is soluble and the silicate layers are swellable .The layered silicate is first swollen in a solvent such as water, chloroform, or toluen. When the polymer and layared silicate solutions are mixed, the polymer chains intercalate and displace the solvent within the interlayer of the silicate. Upon solvent removal, the intercalated structure remains, resulting in a polymer/layered silicate nanocomposite [10].

2.4 Manufacturing Processes of Polymer Nanocomposites

2.4.1 Synthesis of polymer nanocomposites

2.4.1.1 Solution dispersion method

This is based on a solvent system in which the polymer or pre-polymer is soluble and the silicate layers are swellable. The layered silicate is first swollen in a solvent, such as a water, chloroform, or toluen. When the polymer and layared silicate solutions are mixed, the polymer chains intercalate and displace the solvent within the interlayer of the silicate.Upon a solvent removal, the intercalated structure remains, resulting in a polymer/layered silicate nanocomposite [10].

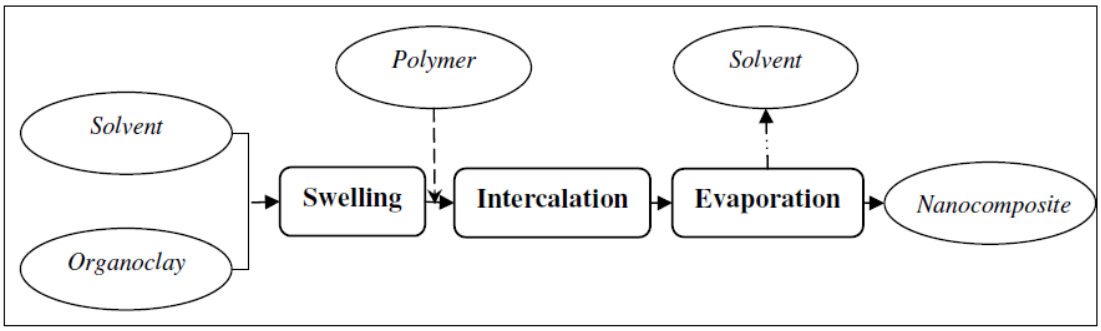

Figure 2.8 : Flowchart of solution method

2.4.2 In-situ polymerization method

In this method, the organically modified layered silicate is swollen within the liquid monomer or a monomer solution so the polymer formation can occur between the intercalated sheets. Polymerization can be initiated either by heat or radiation, by the diffusion of suitable initiator, or by inorganic initiator or catalyst fixed through cation exchange inside the interlayer before selling step [10].

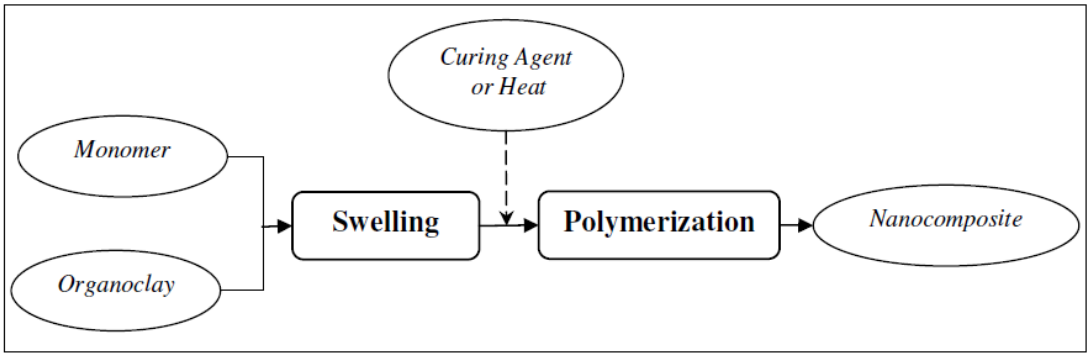

Figure 2.9 : Flowchart of in-situ polymerization

2.4.2.1 Melt-mixing method

This method involves annealing-statically or under shear- a mixture of the polymer and organically modified layered silicate above the softening point of the polymer. This method is environmentally beneficial due to non-availability of organic solvents and it allows the use of polymers that were previously not suitable for in-situ polymerization or solution intercalation [10].

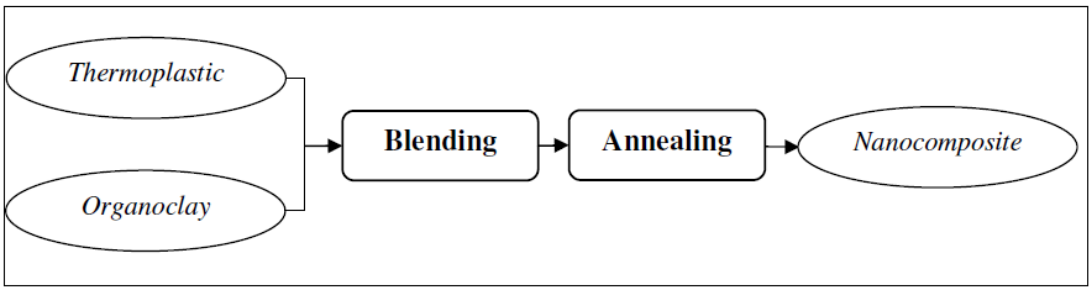

Figure 2.10 : Flowchart of melt mixing method

2.5 Extrusion Process

2.5.1 Extrusion

Polymer melt intercalation is a promising method due to its high productivity, relatively lower cost and compatibility with current polymer processing techniques such as extrusion and injection molding. During extrusion in the processing device, the clay agglomerates are broken up by the external forces and the diffusion of macromolecules into the clay galleries [24]. The extrusion process is not difficult to visualize. A meat grinder is a best model for screw extrusion which is used for plastic processing. The grinder takes a large lump of meat and reduces its size by the screw, mix it all up and then extrude the result through the die. This is a simple

example for extrusion process, but in fact there are several process variables that make it harder to optimize.

Polymer response or behavior in the extruder, combined with the extruder processing conditions, barrel temperatures, screw speed, and screw design, is what allows the extruder to extrude a homogeneous polymer melt at a constant pressure and temperature.

Commonly used continuous screw extruders can be classified in two groups: Single screw and twin screw extruders. The former is the most basic form of extruder that simply melts and forms the material. When compare the this two extuders, twin screw extruders provide excellent meltmixing and are widely used for polymer nanocomposite manufacturing.

2.5.1.1 Twin screw extruder

There are many twin screw extruders commercially available. The choice should depend on the end-use application. Different models have two parallel screw shafts that either rotate in the same direction (called corotating) or rotate in opposite directions (called counterrotating), with varying distances between the screw shafts. If the centerline distance between the shafts is less than the screw diameter, the screws are called intermeshing, whereas screws with a distance between the shafts equal to the screw diameter are called non-inter-meshing.

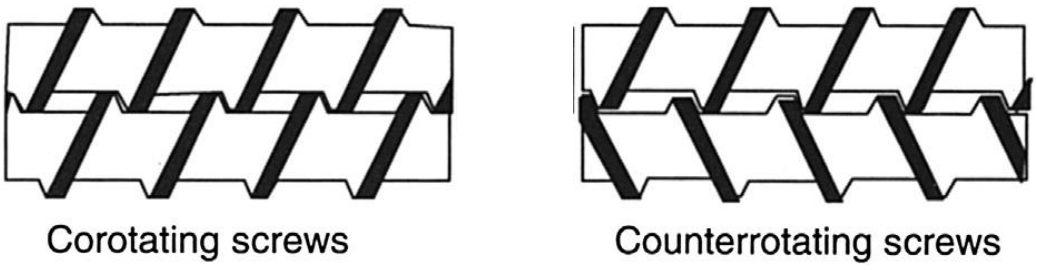

Figure 2.11 : Corotating and counterrotating fully intermeshing screws

Figure 2.6 shows a short segment conveying screw element with parallel corotating and counterrotating screws that are fully intermeshing. In non-inter-meshing extruders, the screw lengths of the two shafts can be equal, or one screw can be longer than the other to provide better pumping capability to the die.

The principal differences in parallel intermeshing and non-inter-meshing twin screw extruders depend on whether the screws are rotating in the same direction, corotating, or in opposite directions, counterrotating, and the distance between the screws.

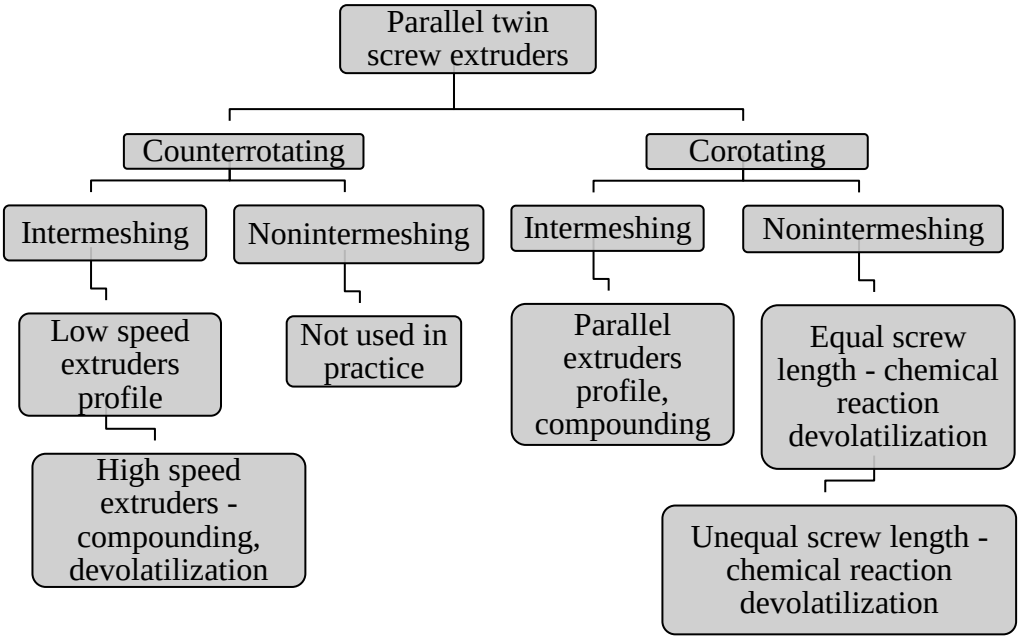

Figure 2.12 : Types of parallel twin screw extruders

High-speed, corotating twin screw extruders are used for compounding resin with additives (colorants, fillers, flame retardants, reinforcements, stabilizers), devolatilization to remove solvents, and reactive extrusion (chemical reactions done in situ in the extruder).

Low-speed corotating and counterrotating extruders are used to produce profiles and pipes. Counterrotating twin screws are used for compounding polyvinyl chloride (PVC) and other resin systems. Non-inter-meshing, counterrotating extruders are principally used for devolatilization and chemical reactions, grafting, polycondensation, addition, feed, screw and barrel, and the die or head) of a parallel twin screw extruder. The fifth component is the control cabinet.

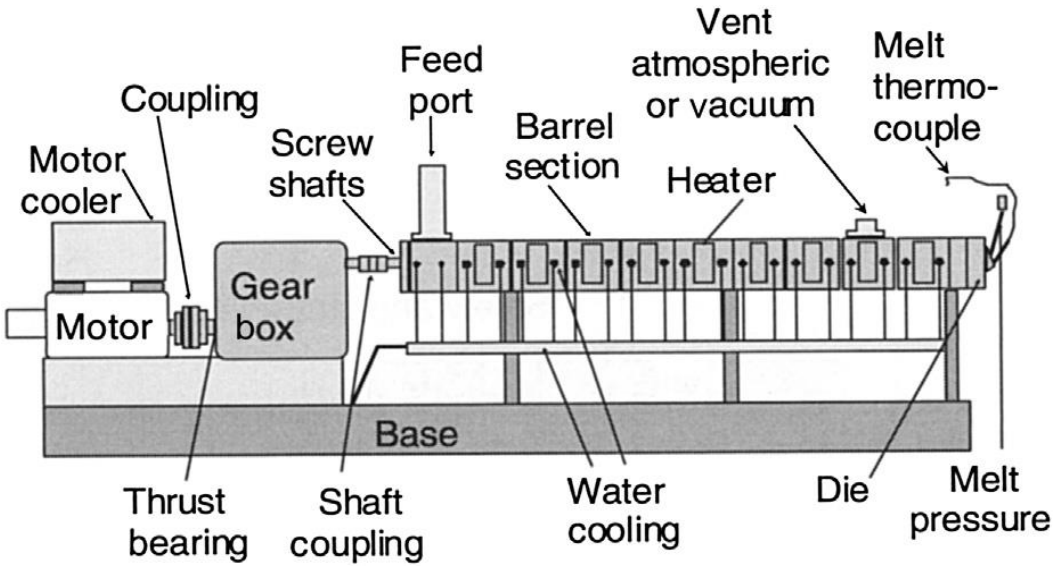

Figure 2.13 : Identification of equipment elements comprising the major components in a twin screw extruder

The various processing parameters of polymers in extruder are defined below.

Practical residence time is the time that polymer, additives, or other formulation components will spend in the extruder from the feed to the die.

Residence time distribution is the shortest to the longest time different particles spend in the extruder.

Dispersion is the breaking up of large particles or agglomerates and their uniform dispersal throughout the melt.

Heat transfer is the ability of the barrel heaters to transfer heat into the material being processed to create a uniform temperature profile throughout the melt.

Venting is the ability of the extruder to remove volatiles or moisture through single or multiple vent ports along the barrel length.

Pumping is the process of delivering a uniform melt pressure and material supply to the die.

Self-wiping is the process of one intermeshing screw element that removes polymer from the adjacent screw element.

Zoning is where specific areas or zones in the extruder accomplish specific extrusion objectives such as melting, mixing, feeding.

Output rate measures the throughput rate or pounds per hour that can be delivered by a specific extruder size or diameter.

Distributive mixing is the process of uniformly distributing all components and melt temperature in the extrudate [25].

2.6 Compatibilizers

Polymeric compatibilizers serve as their name indicates to make compatible the different kinds of materials such as multi component structures. Before discussing the compatibilization of polymer pairs in multi component structures, the compatibility of polymer blends and the compatibilizers will be described. The compatibilization of incompatible polymer compositions is a major area of research and development. The nanoscale dimension, the high aspect ratio and the hydrophilic character of the clays make their dispersion during processing in hydrophobic non-polar polymers such as polyolefins quite difficult. The process of dispersion of clay in polyolefins can be further improved by the addition of a compatibilising agent, for example maleic anhydride (MA) is one of the most widely used vinyl monomers for graft modification of poly-olefins because highly polar maleic anhydride functional group is more compatible with the polar component like modified clay. The dual purpose of these agents is to provide both compatibility with the polymer matrix and enhanced interaction with the organically-modified clays. The degree of compatibility is generally related to the level of adhesion between the phases and the ability to transmit stress across the interface.Mostly, compatibilizers in the form of block and graft copolymers are used for improving interfacial adhesion and reducing interfacial tension [26].

PE compatibilizers can be prepared by copolymer or grafting small polar functional groups like acrylic acid (AA), glycidyl methacrylate (GMA), maleic anhydride (MA), industrial ionomers and itaconic acid (IA) as pendant units or short-chain branches. Among the polar groups, MA has been widely used to prepare PE compatibilizer. Such as polyethylene grafted maleic anhydrate (PE-g-MA) and polytethylene copolymer maleic anhydride (PE-co-MA). Other widely used to polyolefins as a compatibilizer is PP. Polyolefins of PP the absence of polar groups in the chain, direct intercalation or exfoliation in the silicate galleries is very difficult. Efforts were made to improve the compatibility of clay with PP by using functional

oligomers as compatibilizer. PP nanocomposites using a functional oligomer with polar telechelic OH groups as a compatibilizer. Several studies report the use of maleic anhydride grafted PP as a compatibilizer. In both cases the interaction between filler and polymer is enhanced by a strong hydrogen bonding between OH or COOH groups and the oxygen groups of silicate. Following this idea, studies were reported where different modifiers based on PP oxide maleic terminated are used to treat the silicate surface. In this situation, the Na^+ is kept inside the silicate galleries and a dipole–dipole interaction occurs between the silicate and the modifier.

2.6.1 Maleic anhydride grafted polyethylene: (PE-g-MA)

Polyethylene (PE) grafted with maleic anhydride (MA), PEgMA, exhibits enhanced compatibility in polymer alloys of PE with polar materials like cellulose and montmorillonite [27], which are promising as new environmental protection plastics. However, the lack of well-confirmed experimental evidence has left obscure the molecular structure of MA group grafted onto PE, mainly owing the low graft degree[28]. Maleic-anhydride-grafted polyethylene (PEgMA)/clay nanocomposites were also prepared using melt intercalation technique [29].

2.6.2 Maleic anhydride grafted PP (PP-g-MA)

It was used as one of the commercial compatibilizers which is a maleic anhydride functionalized polypropylene (PPgMA), containing 1 wt% of maleic anhydride. Acid value is 41 mg KOH/g. Density and viscosity of PP-g-MA are 0.93 g/cm3 (at 23 ^{0}C) and 1100 mPa.s, respectively. Also softening point is approximately 161 ^{0}C.

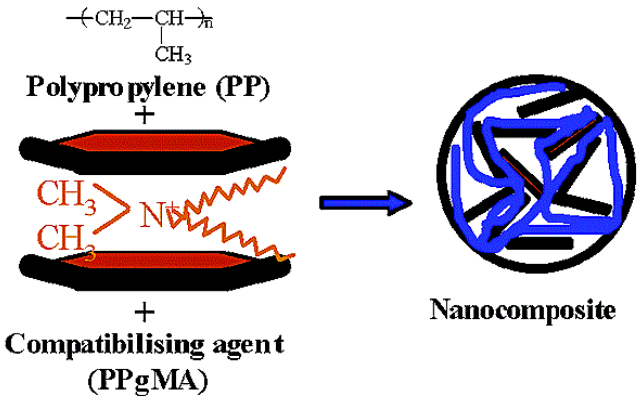

Figure 2.14 : Interaction between PP-g-MA and clay

2.7 Literature Review

Garmabi and co-worker analyzed the effects of some material properties on mechanical properties of the prepared LDPE/LLDPE/Nanoclay nanocomposites by lab-scale twin-screw extruder. A maleic anhydride modified linear low density polyethylene with a maleic anhydride content of 0.2–2.0 wt% was to be used as a compatibiliser. The enhanced tensile properties, improved ductility and modulus were obtained as a result of good interfacial interaction [30].

Gunning and co-workers investigated the effect of maleic anhydride grafting efficiency on the bending properties of polyethylene nanocomposites. In this study the results from XRD scans showed that increased intercalation in polymer nanoclay composites was achieved by increasing the grafted MA content [31].

Extruded films of low density polyethylene and chitosan mixtures with the addition of polyethylene-graft-maleic anhydride as a compatibilizer for the blends, and glycerol, as a plasticizer for chitosan were prepared by Rodríguez-Félix and co-workers. The use of compatibilizer and plasticizer agents improved the processability and compatibility of the mixtures, as well as their mechanical properties, as revealed by mechanical property measurements and scanning electron microscopy (SEM).

The addition of a compatibilizer into polyethlene/chitosan blends , polyethylene with grafted maleic anhydride, allows easy workability of the polyethylene/chitosan mixtures into films in standard extrusion equipment. The use of an anhydride-based coupling agent, extensively used to compatibilize polymer blends, was effectively extended to improve the mechanical properties of chitosan composites [32].

Seyidoglu and co-worker were prepared modified clays and their use in polypropylene-based nanocomposites. The use of modified bentonite as a reinforcement in polypropylene (PP)/organoclay/maleic anhydride grafted polypropylene (PPgMA) nanocomposites was investigated. Bentonite were modified with two quaternary ammonium salts: dimethyl dioctadecylammonium chloride [DMDA][Cl] and [TKA][Br], and one quaternary phosphonium salt: tributyl hexadecyl phosphonium bromide [TBHP][Br], in order to observed effects of modified surface between polyolefins to presence compatibilizers. They investigated mechanical properties. Their results show that young's modulus of PP was increased

by 30% with DMDA and 9% with TBHP. The yield strength of PP was increased by 15% with DMDA and 8.3% with TBHP [33].

Choi and co-workers investigated polypropylene (PP)/clay nanocomposites based on PP, organic clay (montmorillonite; MMT), and maleated polypropylene (PP-g-MA) were prepared by extruded compounding. The mechanical, thermal, morphological, and gas barrier properties of the resulting PP/clay nanocomposites were considered at varying concentrations by Choi and co-workers. The results revealed that the mechanical strengths, including tensile, flexural, and Izod impact strength, were increased for PP/clay nanocomposites compared to neat PP. The thermal properties illustrated a tendency for the melting and degradation temperatures to increase with the clay concentration. The results from XRD scans showed thah nanocomposites revealed increased *d*-spacing of the MMT layers, definition that the compatibility of neat PP and clay was improved by the addition of PP-g-MA , and the intercalation and partial exfoliation of the layers [34].

Jahani analyzed the effect of filler types of mica and talc on the rheological properties, mechanical properties , and morphology of the chemically coupled polypropylene composites is studied in this work. The maleic anhydride grafted polypropylene (PP-g-MA) was used as an adhesion supporter for coupling mineral particles with the polypropylene matrix. The samples were prepared by a twin screw extruder. The tensile tests carried out on the injection molded samples showed a reinforcing effect of talc up to 20wt% on the polypropylene (PP). The tensile strength of PP-mica composites showed a slight decrease at all percentages of mica. The effect of chemical coupling by using PP-g-MA on the tensile strength was more obvious in increasing the tensile strength for PP-mica than PP-talc composites [35].

Mauler and co-workers were studied of the mechanical properties of polypropylene-based nanocomposite via the addition of a combination of organoclays. The properties of polypropylene (PP) nanocomposites are dependent on the quaternary ammonium salt in the montmorillonite (MMT). They prepeared two different modified MMT. A nanocomposite with C-15A, which has a high cation exchange capacity (CEC), exhibits an increase in its impact properties, while one prepared with C-20A, which has a low CEC, shows an increase in the flexural modulus. In order to achieve improving in both properties, PP nanocomposites were prepared using a combination of 1:1 of C-15A/C-20A. X-ray, TEM, thermal properties, dynamical

mechanical analysis (DMA), and mechanical tests were used to evaluate the properties of this novel mixture. Nanocomposites of partially exfoliated morphology were obtained, especially when 5 wt% of (PP-g-MA) was used as compatibilizers. The mechanical tests illustrated that the use of a 1:1 mixture of C-15A/C-20A caused a simultaneous gain of approximately 12% in flexural modulus and a five times higher impact strength. The DMA results showed that while the organoclay improved the modulus of PP, the Tg was decreased slightly [36].

Wang and co-worker were prepared PMMA/clay nanocomposites with styrene-maleic anhydride (SMA) copolymers. They were investigated the effect of copolymer type of compatibilizers on thermal, mechanical and dielectric properties. When they prepared the nanocomposites consist of the clay content was 5 wt% for each nanocomposite. The SMA content was 15 wt% for SMA modified systems. As mesaured results by XRD, the organoclay was well intercalated in the PMMA matrix. The TEM studies clearly showed that the MMT clay was intercalated and randomly dispersed in the polymer nanocomposites materials [37].

3. EXPERIMENTAL PART

3.1 Materials

3.1.1 Low density polyethylene (PE)

Low density polyethylene was obtained from Dow Chemical Company DOW™ LDPE 780E. The melt flow rate (190°C/2.16 kg) is 20 g/10min. The density is declared 0.923 g/cm³ by the company.

3.1.2 Polypropylene (PP)

Polypropylene was obtained from Impact incorporated. The melt flow rate (190° C/2.16 kg) is 29 g/10min. The density is declared 0.89 g/cm³ by the company.

3.1.3 Polyethylene grafted maleic anhydride

Bondyram® 4108 is a maleic anhydride modified linear low density polyethylene recommended for coupling of polyethylene and other fillers in PE composites. The melt flow rate (190°C/2.16 kg) is 1.5 g/10min. Maleic anhydride grafting level is ~ 1%.

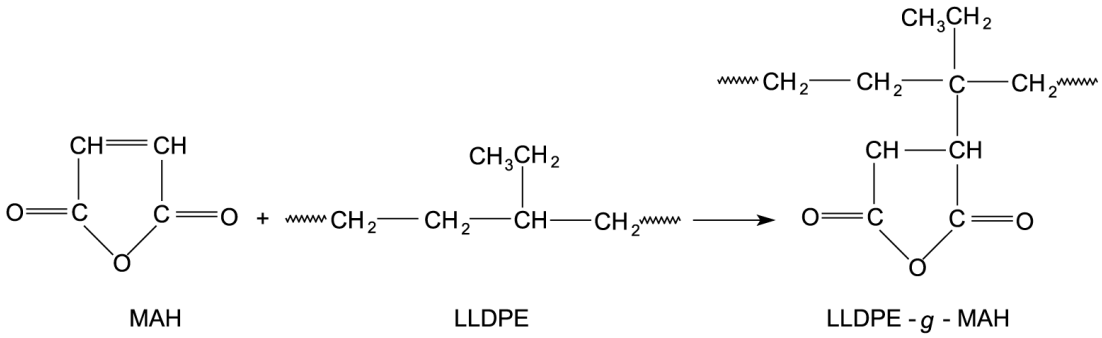

Figure 3.1 : LLDPE grafted maleic anhydride

3.1.4 Polypropylene grafted maleic anhydride

Bondyram® 1001 is a maleic anhydride modified polypropylene recommended for coupling of polypropylene and other fillers in PP composites. The melt flow rate (190°C/2.16 kg) is 100 g/10min.

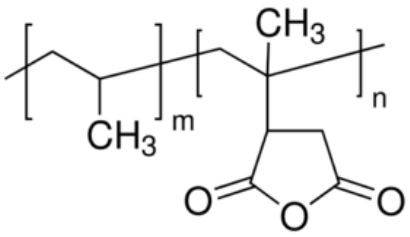

Figure 3.2 : Polypropylene grafted maleic anhydride

3.1.5 Polyethylene copolymer maleic anhydride

ZeMac® Vertellus M601 copolymers are 1:1 copolymers of ethylene and maleic anhydride which are excellent film formers and compatibilizing agents.

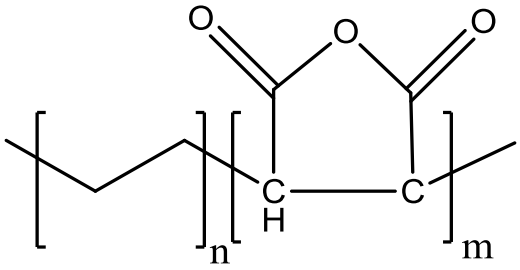

Figure 3.3 : Polyethylene copolymer maleic anhydride

3.1.6 Clay

In this study two types of modified clays were used; Nanomer® I-30 and Nanomer® I-44. They were supplied by Nanocor, USA. Nanomer® nanoclays have high purity, and surface compatibilized. Montmorillonites are suitable for using in a wide variety of plastics. This technical data sheet describes patented Nanomer grades specifically designed for polyolefin applications. For use in polyolefins, Nanomer grades are based on two different clays surface treatment chemistries. These products are fine free flowing powders. Typically, they have mean particle sizes in the range of 15-20 μm.

I-30 (primary amine) is octadecly Amine.

Chemical Formulation is ; $CH_3(CH_2)_{16}CH_2NH_2$

This clays modifier concentration 25-30 wt%.

I-44 (quaternary ammonium) is Di-methyl di-hydrogenated tallow ammonium. This clays modifier concentration 25-30 wt%.

Chemical Formulation is Figure 3.4

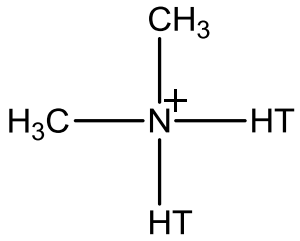

Figure 3.4 : Quaternary amonium

Table 3.1 : Properties of Nanomer® Products

Product	Dispersion	Heat Stability	Mechanical	FR	Electrochemical
I.30P	Good	Excellent	Yes	Yes	Excellent
I.44P	Excellent	Good	Yes	Yes	Good

3.2 Equipments

3.2.1 Extruder

Melt compounding was conducted with Poex T-27 T fully intermeshing and co-rotating twin screw extruder having an L/D ratio of 48 with diameter of 27 mm and screw length of 1296 mm. Extruder has a maximum 30 kW motor power and 1200 rpm maximum screw speed.

Barrel temperatures were set to the desired processing temperatures by using several temperature controllers on the control panel and allowed to stabilize prior to experiments. A picture of the twin screw extruder is presented in Figure 3.5 and properties are summarized in Table 3.2.

Table 3.2 : POEX T-27 Twin screw extruder technical specifications

	Units	POEX T-27
Screw diameter	mm	27
Maximum screw speed	rpm	1200
L/D (shaft length/screw diameter)	-	48:1
Working length	mm	1296
Max. capacity	kg/h	5-100
Motor power	kW	30
Heating power	kW	12
Average water requirement	lt/min	30
Height	mm	1000
Total weight	kg	950
Max. pressure	bar	300
Vacuum pump	kW	0,75
Cooling unit (pump)	kW	0,50
Granulating motor	kW	2,2

Figure 3.5 : Twin screw extruder

During the melt compounding, materials were fed from the main and side feeders according to order of addition. Materials were melt and mixed in the extruder and the molten product was purged from the die and passed through the water bath for cooling. Wet product was subjected to air through an air knife attached to the end of the water bath in order to remove the excess water. Then, the product was pelletized by granulating unit. Granulating unit is shown in Figure 3.6.

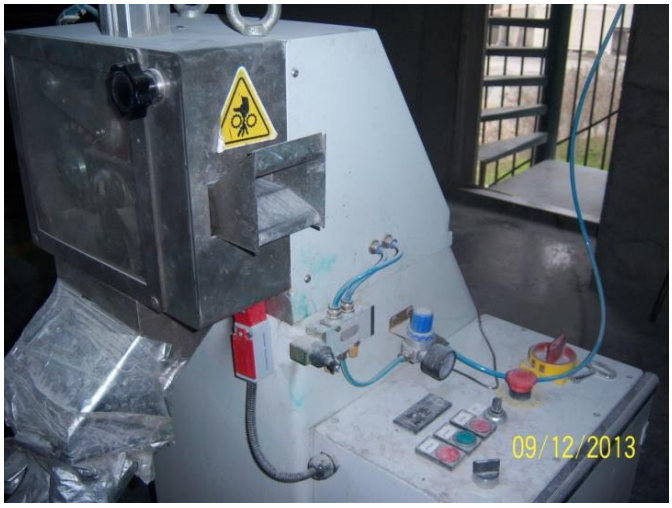

Figure 3.6 : Granulating unit

3.2.2 Injection molding machine

Arburg injection machine was used to produce some samples according to ISO 527 standard as shown in Figure 3.7. Injection unit consists a hopper, a heat controlled barrels-cylinder, a screw and a motor. Technical specifications of the Arburg injection machine are given in the Table 3.3.

Figure 3.7 : Arburg injection molding machine

Table 3.3 : Arburg injection molding machine technical specifications

Specification	Unit	Arburg
Screw diameter	mm	27
Max. injection pressure	bar	950
Wax. Shot weight	g	78
Hydraulic motor power	W	1800
Max. clamping force	tonnes	20
Screw back pressure	bar	20

3.2.3 X-ray diffraction (XRD)

X-Ray diffraction analysis of clays and nanocomposites were made by Panalytical X'Pert Powder XRD. The X-ray diffraction pattern was recorded on the imaging plate, and the intensity of each reflection was estimated by two-dimensional measurement and subsequent background removal. X-Ray diffraction (XRD) patterns of the samples were recorded by monitoring the diffraction angles (2θ) from 2° to 20° on the diffractometer, using CuKα radiation. The wavelength used was λ= 1.5405 Å.

3.2.4 Differential scanning calorimetry analysis (DSC)

Thermal analysis of the samples were done with TA Instruments Q20 DSC Differential Scanning Calorimetry machine as shown in Figure 3.8. The analysis were done for all blends between 25ºC and 300ºC at 10ºC/min heating rate under nitrogen atmosphere. Melting temperatures (T_m), crystallization temperatures (T_g), the enthalpy of melting, the enthalpy of crystallization and % crystalinity values of the compounds were obtained from a differential scanning calorimeter (DSC).

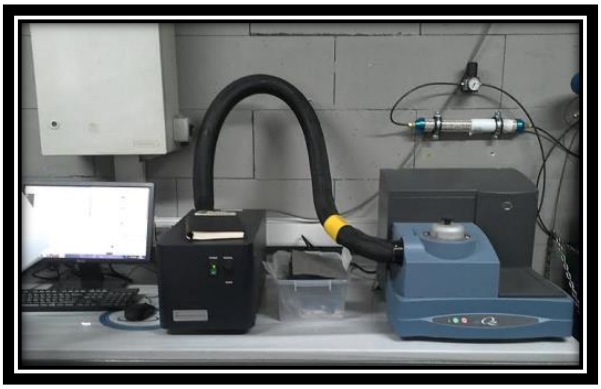

Figure 3.8 : Differential scanning calorimetry analysis

Table 3.4 : Q20 DSC aparatus properties

Temperature Range	Max. 725 ^{0}C
Cooling Aparatus and Temperature Range	-40 ^{0}C – 725 ^{0}C
Temperature Sensitivity	+/- 0.1 ^{0}C
Dynamic Measurement Range	+/- 350 mW
Sensitivity	1.0 µW
Calorimetric Sensitivity (indium)	+/- 0.1 %
Indium Length/width(mW/^{0}C)	8.0
Test Standard	ISO-11357-1

3.2.5 Furnace

NUVE MF 210 model furnace has a maximum working temperature of 800°C. The furnace was used the determine inorganic ingriedients percentages.

3.2.6 Universal testing machine

Tensile properties of specimens were measured by Lloyd LC universal tensile testing machine equipped with 5 kN load cell as load indicator and long stroke extensometer as an extension indicator. Testing speed was set to 50 mm/min and gauge length (L_o) was set to 100 mm. Tensile testing machine is presented in Figure 3.9.

Figure 3.9 : Universal tensile testing machine

3.2.7 Izod impact test machine

Izod impact strength of specimens was measured by Ceast 9050 Izod impact machine which could operate between 0.5 and 25 Joule energy range as shown in Figure 3.10.

Figure 3.10 : Izod impact testing machine

3.2.8 Shore-D hardness test device

Shore-D hardness of samples was measured by Zwick Shore-D durometer with ASTM D 2240. Easy readable scale of the device is between 0-100 digit. This portable device provides us highly sensitive Shore-D hardness values.

Figure 3.11 : Shore-D hardness measure device

3.2.9 Melt flow index (MFI) apparatus

Melt flow index is the output rate (flow) in grammer that occurs in 10 minutes through a standard die of 2.095 ± 0.005 mm diameter and 8.000 ± 0.025 mm in length when a fixed pressure is applied to the melt via a piston and a load that is predefined according to the polymer type at a fixed temperature. Melt flow index (MFI) was measured by Ceast Modular Base Model testing machine as shown in Figure 3.12

Figure 3.12 : Melt flow index machine

3.2.10 Density determination kit

The density of specimens was measured with Radwag Was 220/X density scale as shown in Figure 3.13

Figure 3.13 : Density determination kit

3.2.11 Glow wire tester

Glow wire test was carried out by using PTL Glow – wire test apparatus to determine the fire resistance. This test method measures and describes the response or materials, products, or assemblies to heat and flame under controlled conditions, but does not by itself incorporate all factors required for fire hazard or fire risk assessment of the materials, products, or assemblies under actual fire conditions. PTL Glow wire test apparatus is equipped with glow wire, thermocouple, temperature indicator, supply circuit, text fixture, indicator board and test chamber as shown in Figure 3.14.

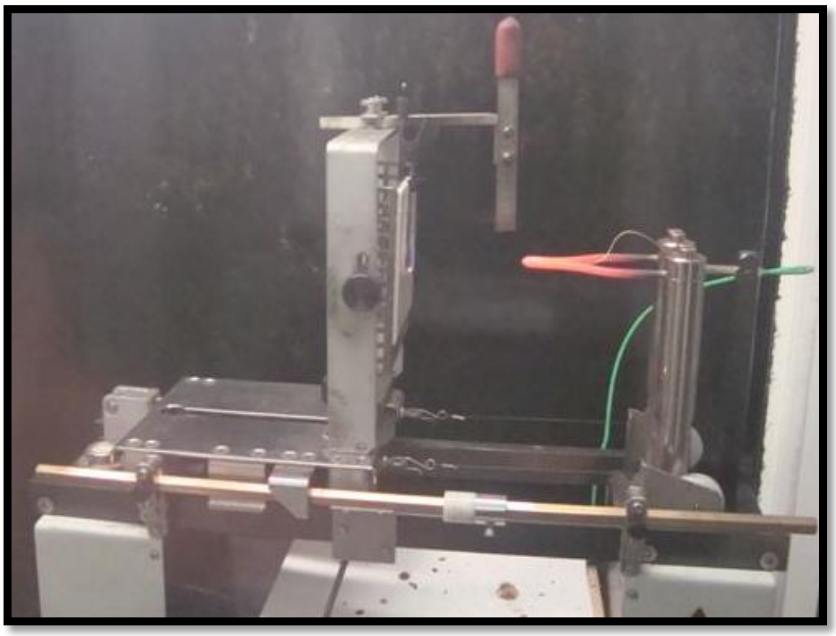

Figure 3.14 : Glow wire tester

3.3 Experimetal Procedure

3.3.1 Preparation of nanocomposites (PNC)

Nanocomposites having different compositions of polyethylene or polypropylene matrix, modified clay and compatibilizer were prepared by melt compounding method by extrusion, and then were injection molded for analysis. It this study, the effects of two different organoclays and two different compatibilizers were investigated on the nanocomposites produced. The organoclay content was kept constant as 5wt%. PE-co-MA is a new compatibilizer. Thus, the proper content was examined by preparing 5wt%, 10wt% and 15wt% PE-co-MA containing nanocomposites. As it is known by earlier studies of PE-g-MA compatibilizer in nanocomposites, the best result was obtained in addition of 15wt% PE-g-MA for 5wt% organoclay. Nanocomposite formulations were given in Table 3.5.

Polymer matrix, compatibilizers and clays were mixed previously and then fed from the main feeder of the twin screw extruder. Total feeding rate of the materials was set to 25 g/min and kept constant during the study. The nanocomposite product was cooled by passing through a water bath, and the wet product was dried by an air knife after the water bath, and then the product was pelletized. The temperature profile chosen for PE or PP was 70°C/170°C /170°C /175°C /185°C /185°C /190°C /190°C

/195°C /195°C /205°C /210°C /210°C from hopper to die, respectively. Screw speed was chosen as 350 rpm in order to disperse PE or PP nanocomposites.

Table 3.5 : Formulations of nanocomposite samples (weight per cent)

Samples	PE	PP	PE-co-MA	PE-g-MA	PP-g-MA	I-44	I-30
PE	100	–	–	–	–	–	–
90PE/5PEcoMA/5I-44	90	–	5	–	–	5	–
90PE/5PEcoMA/5I-30	90	–	5	–	–	–	5
85PE/10PEcoMA/5I-44	85	–	10	–	–	5	–
85PE/10PEcoMA/5I-30	85	–	10	–	–	–	5
80PE/15PEcoMA/5I-44	80	–	15	–	–	5	–
80PE/15PEcoMA/5I-30	80	–	15	–	–	–	5
80PE/15PEgMA/5I-44	80	–	–	15	–	5	–
80PE/15PEgMA/5I-30	80	–	–	15	–	–	5
100PP	–	100	–	–	–	–	–
90PP/5PEcoMA/5I-44	–	90	5	–	–	5	–
80PP/15PEcoMA/5I-44	–	80	15	–	–	5	–
80PP/15PPgMA/5I-44	–	80	–	–	15	5	–

3.4 Tests and Analyses

3.4.1 X-ray diffraction (XRD)

The XRD patterns of polyethylene nanocomposites containing different modified clay show diffraction peaks all shifted to lower 2θ degrees against the peak of

modified clays, which indicates the increasing of layers spacing due to the intercalation or exfoliation. Bragg equation ($\lambda n = 2 d \sin \theta$; $n=0,1,2,...$) is the well-known fundamental law of x-ray crystallography. Interplanar spacing is d, the angle between the planes and the direction of the beam is θ, λ is wavelength used light and n is integer. The angle between reflected wave and solid surface is θ.

3.4.2 Thermal testing

3.4.3 Differential scanning calorimetry analysis (DSC)

Sample preparations for DSC analysis were implemented by cutting a piece of material from the middle section of the injection molded specimens. For each composition, about 7.5-15 mg material was replaced in aluminum pans and heated from 25 ºC to 300 ºC at a rate of 10ºC/min under nitrogen atmosphere. Melting temperatures (T_m), crystallization temperatures (T_c), the entalphy of melting, the enthalpy of crystallization and percent crystalinity (% X_c) values of the compounds were obtained using a differential scanning calorimeter (DSC).

3.4.3.1 Ash testing

For each composition, approximately 2-2.5 material was replaced in porcelain crucible and heated from 800 ºC.

3.4.4 Mechanical testing

3.4.4.1 Universal testing machine

Tensile properties of polymeric compounds were investigated by using tensile test specimens described as test specimens 'Type One' according to ISO / R 527. Normal specimens were used to measure tensile properties. The test was carried out at standard conditions at 23 ± 2°C.

Tensile properties of the samples were measured by Lloyd LC universal tensile testing machine. Testing speed was set to 50 mm/min and gauge length (L_o) was set to 100 mm. Tensile strength, modulus of elasticity, and elongation and strength at break were calculated from the tensile measurements. Tensile strenght is a measure of the material's strength under tensile loading. The modulus is a measure of material's resistance to deformation and can be found by the initial slope of the

stress-strain curve. Stretch limit of the material or deformation limit before its break is called elongation.

3.4.4.2 Izod impact tester

Izod impact strength of specimens was determined according to ISO 180/1A standard. The thickness and width of the samples were measured by screw micrometer reading. Then, 2 mm-notch was opened by using manual notching machine. The specimen was placed into test machine grips in such a way that the notched surface was faced to the impact point. The pendulum was then released and the impact energy was recorded after making correction for frictional losses. The Izod impact strength, in kilojoules per square meter (KJ/m^2), as calculated as follow:

Izod Impact Strength = A_k / (X x Y_k) x 10^3

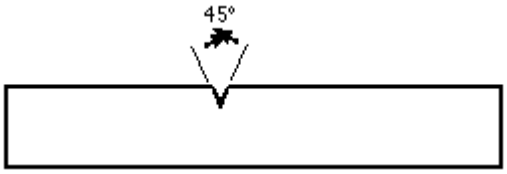

Figure 3.15 : Izod test specimen

Where A_k is the impact energy, in joules, absorbed by the test specimens and it is corrected for frictional losses. X is the thickness, in millimeters, of specimen. Y_k is the difference of width and notch depth, in millimeters.

3.4.4.3 Hardness

The samples prepared in extruder are used for hardness test. As per standard measurement (ASTM D 2240); both initially measured value and 20 seconds later one are recorded. Two parallel values are measured for each sample and then averages of the values are calculated and recorded.

3.4.5 Melt flow index (MFI) apparatus

Melt flow index is an assessment of average molecular mass; is an inverse measure of the melt viscosity and is used to specify the flow behavior of molten polymer which is defined as an important factor affecting the processability of polymers. Melt flow index is the output rate (flow) in grammes that occurs in 10 minutes through a standard die of 2.095 ± 0.005 mm diameter and 8.000 ± 0.025 mm in length when a

fixed pressure is applied to the melt via a piston and a load that is predefined according to the polymer type at a fixed temperature.

The flow behavior of molten polymer is defined as an important factor affecting the processability of polymers. Melt flow index (MFI) or melt flow rate (MFR) is described by flow properties of the molten polymers and measured as per ISO 1133 test standard.

The test temperature and weight are set to 230°C and 2.16 kg. The densities of samples are used for measurement. After cleaning the cylinder and piston, injection molded-test samples are fed into the preheated cylinder. The material is compressed by hand pressure to ensure the charge is free from air during charging. The molten polymeric material is discharged from the die.

3.4.6 Density

The density of specimens is determined as per the procedure described in ISO 1183. This method is worked according to "Archimedes Principles of Density Measurement" and specific gravity. Specific gravity refers to the ratio of the density of a sample to the density of pure water.

The density of specimen depends on the weight of the sample in air, weight in liquid and the density of the liquid. ρ : Density of sample, A : Weight in air, B: Weigt in liquid, ρ_0: Density of liquid.

$$\rho = (A/A\text{-}B)* \rho_0 \qquad \textbf{(3.1)}$$

3.4.7 Glow wire tester

The glow wire of specimens was determined according to the procedure explained in ASTM D6194. Test specimens were kept at temperature of 23 ± 2°C and 50 ± 5 % relative humidity for at least 40 hours prior to testing. Thickness of specimens must be 0.25 mm or greater than 6.4 mm.

The specimen was mounted in the test so that the surface that comes in contact with the tip of the glow-wire was vertical and any losses to supporting means were insignificant. The pre-selected glow-wire temperature was maintained for at least 60 seconds prior to conducting the test. The specimen was brought in contact with the

tip of the glow-wire at an applied force of 1.0 ± 0.2 N for 30 ± 1 s. For the purpose of this test, ignition will be deemed to have occurred in case of either sustained flaming occurs or the tissue paper on the indicator board placed underneath the apparatus exhibits flames caused by particles falling from the test specimen.

4. RESULTS AND DISCUSSION

4.1 Morphological, Thermal and Mechanical Properties

4.1.1 XRD

The results of the XRD measurements of nanoclays and PE nanocomposite samples are given in Figure 4.1, 4.2, 4.3, and Table 4.1. From the diffraction values, the distance between clay layers (d_{001}) of nanocomposites was calculated from the Bragg equation. The XRD measurements were applied to the 15wt% compatibilizer containing samples, because the significant improving of clay dispersion was expected for these samples. 80PE/15PEcoMA/5I-30 and 80PE/15PEgMA/5I-30 samples consisting of I-30 showed the best layer spacing. The partial exfoliation was observed for these samples due to the d_{001} values were measured as greater than 40 Å.

Table 4.1 : XRD measurements results of the samples

Samples	d_{001} (Å)
80PE /15PEcoMA/5I-44	35.1
80PE/15PEgMA/5I-44	34.1
80PE/15 PEcoMA /5I-30	46.1
80PE/15PEgMA/5I-30	41.0
I-44	25.8
I-30	20.9

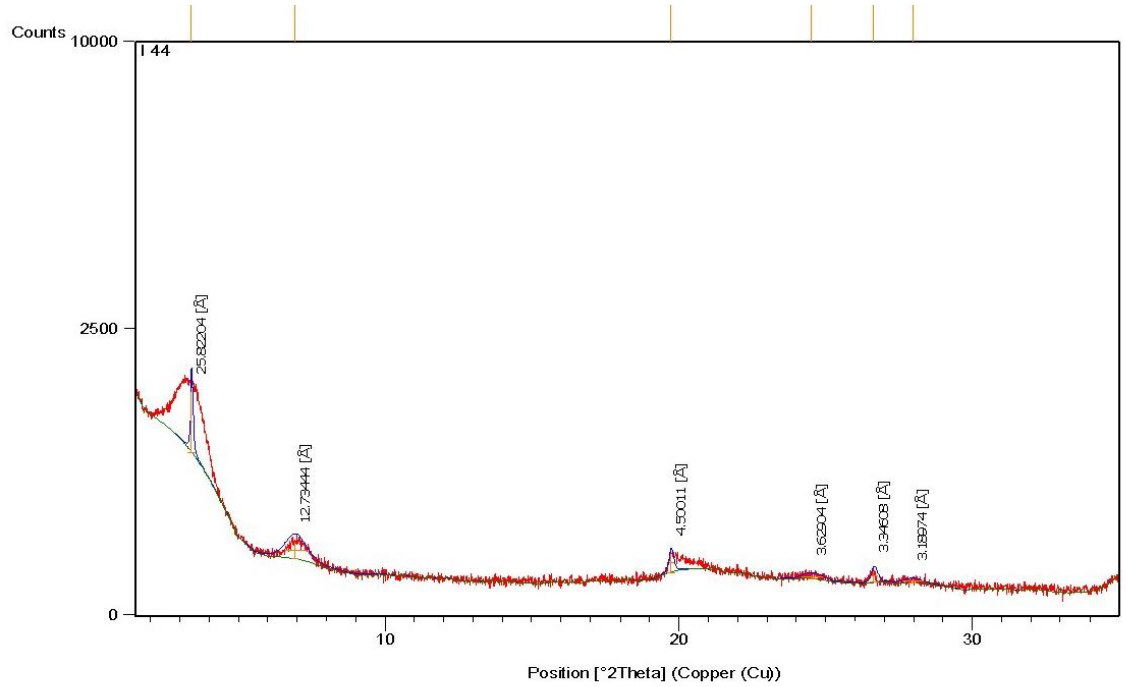

Figure 4.1 : XRD patterns of I-44 clay

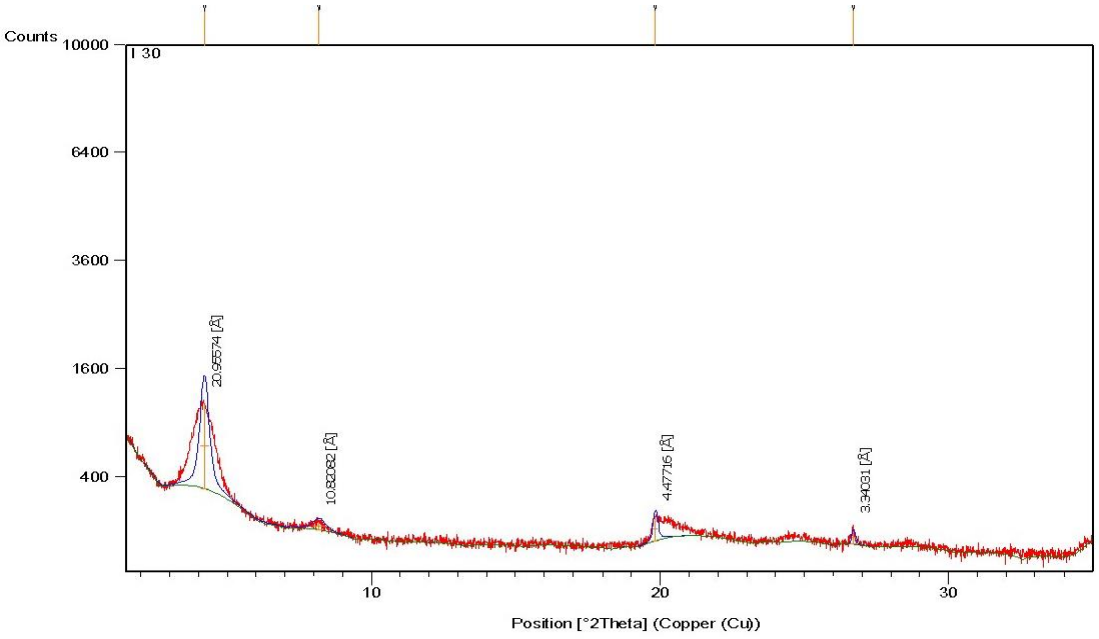

Figure 4.2 : XRD patterns of I-30 clay

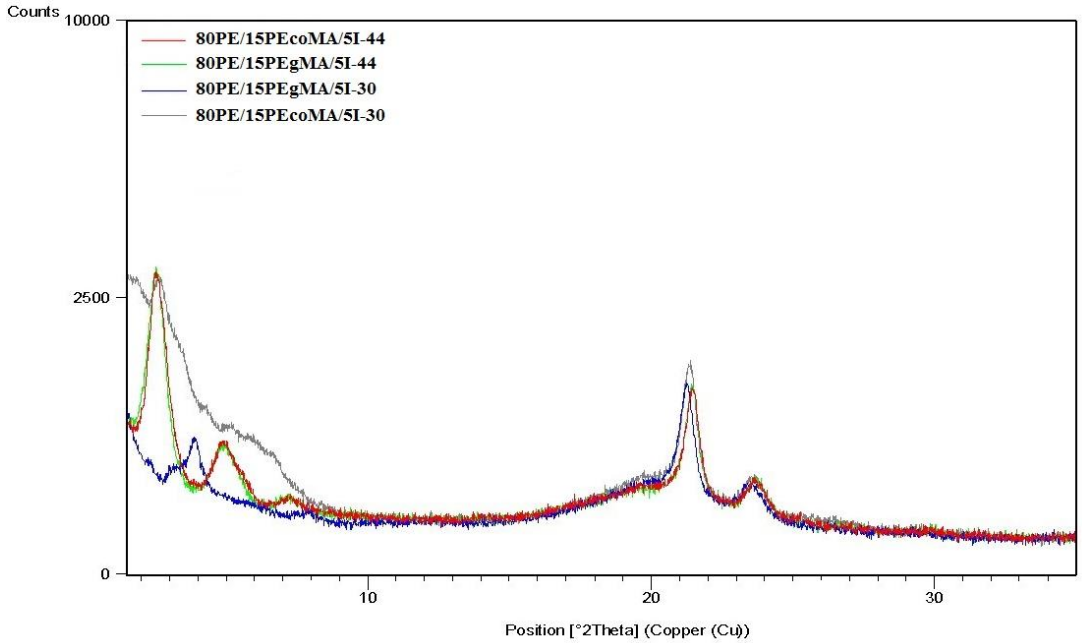

Figure 4.3 : XRD patterns of polymer nanocomposite samples that contain 15wt% compatibilizer, clay and 80 wt% PE matrix

4.1.2 Thermal testing

4.1.2.1 DSC

DSC analysis was conducted to determine the crystallization behavior of polyethylene, polypropylene and the effects of organoclays and compatibilizers on crystallization during nanocomposite preparation. The DSC results were given in Figure 4.4 and 4.5. The T_c (peak), T_c (onset) T_m (peak), T_m (onset) values were determined from these figures and given in Table 4.2. The percent crystallinity values of each phase were calculated as the ratio of the heat of fusion of the sample (ΔH_m), divided by the weight fraction (w) of the polymer in the nanocomposite and the heat of fusion of the pure crystalline form of the polymer. The heat of fusion data for pure crystalline form of PE (ΔH^o_m), and PP (ΔH^o_m), were taken as 293 J/g and 207 J/g, respectively. The percent crystallinity ($\%X_c$) were calculated from the equation 4.1.

$$\%X_c = [\Delta H_m/\Delta H°_m * w] * 100 \qquad \textbf{(4.1)}$$

Table 4.2 represents the heat of fusion, melting temperatures and % crystallinity values of PE, PP and their nanocomposites. Addition of organoclay decreases the crystallization temperature and increases the number of crystallite. The increasing trend in crystallinity values, which is observed as the compatibilizers content increases, is also seen in the nanocomposites at same organoclay content loading.

The increase in crystallinity values of the I-44 type and I-30 type organoclay loaded nanocomposites is observed better with 15 wt% compatibilizer content. As expected, as dispersion of nanocomposites increases, the % crystallinity also increases. The results are attributed to the well dispersion of the organoclay platelets owing to high interaction with I-30 at 15wt% compatibilizer loading.

Table 4.2 : Test results of DSC measurements of samples

Samples	T_c (peak) (°C)	T_c (onset) (°C)	T_m (peak) (°C)	T_m (onset) (°C)	ΔH_c (J/g)	ΔH_m (J/g)	$\%X_c$
100PE			115			95.7	32.7
90PE /5 PE-co-MA /5 I-44	100.1	103.7	114.0	101.2	73.2	85.3	30.6
90PE /5PE-co-MA /5 I-30	99.0	102.8	114.4	101.9	57.0	74.5	26.8
85PE /10 PE-co-MA /5 I-44	99.7	103.3	115.0	102.9	70.0	89.9	36.1
85PE /10 PE-co-MA /5 I-30	100.4	103.6	112.1	102.3	67.8	94.1	37.8
80PE /15 PE-co-MA /5 I-44	101.3	104.1	113.9	104.4	76.5	91.0	39.0
80PE /15 PE-g-MA /5 I-44	101.2	104.3	113.7	104.1	66.9	89.6	38.2
80PE /15 PE-co-MA /5 I-30	99.4	103.2	115.5	103.7	100.5	106.1	45.2
80PE /15 PE-g-MA /5 I-30	99.5	102.7	113.8	102	94.1	104.0	44.4
100PP			165.1			84.1	40.6
90PP /5PE-co-MA /5 I-44	115.7	121.2	166.7	152.5	91.0	80.7	43.3
80PP /15 PE-co-MA /5 I-44	115.9	121.8	164.6	148.7	129.3	102.8	62.1
80PP /15 PP-g-MA /5 I-44	118.6	123.7	164.6	150	105.7	95.5	57.6

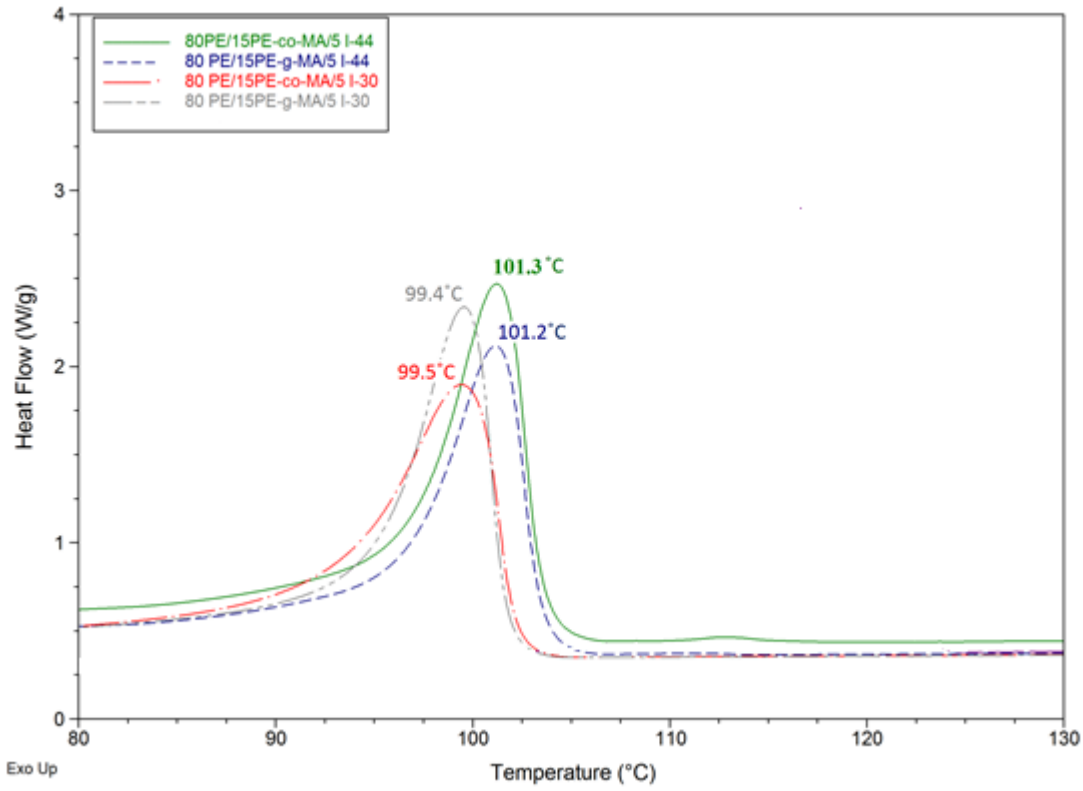

Figure 4.4 : Comparison of T_c for 80wt% content of PE

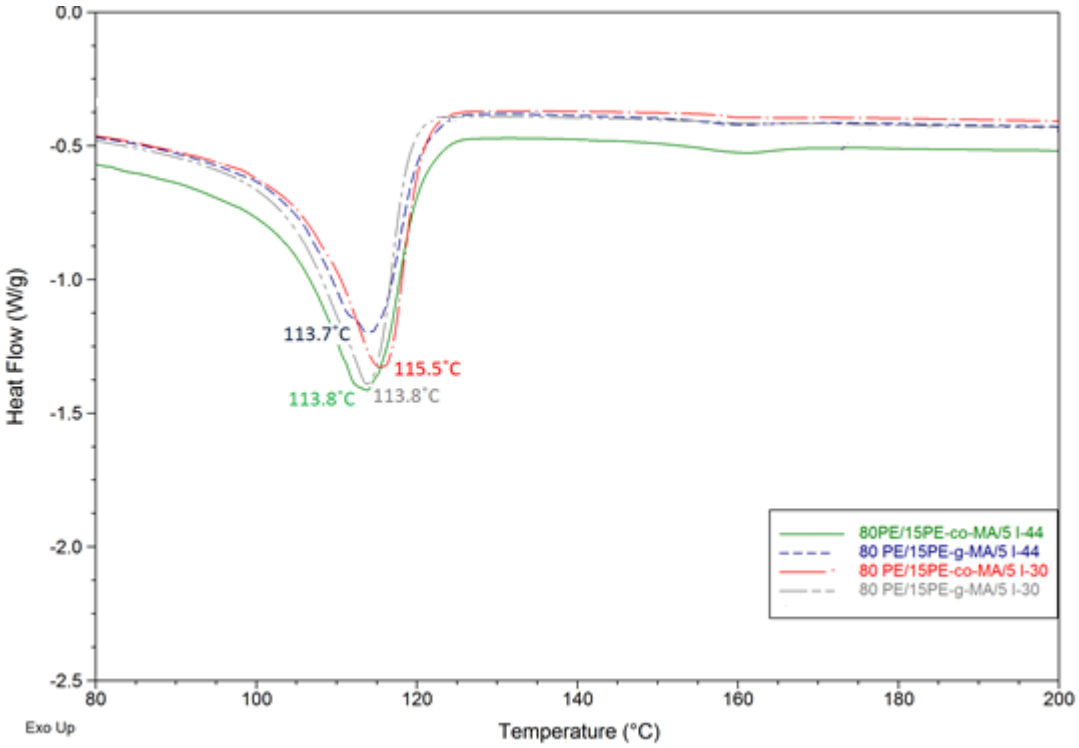

Figure 4.5 : Comparison of T_m for 80wt% content of PE

4.1.2.2 Ash testing

In PE/clay nanocomposites (I-30 and I-44) and PP/clay nanocomposites (I-44), the 5wt% of clay (I-30 and I-44) were used. In order to support this, Ash test was used and this measurements are given in Table 4.3. The residues weighed and ash content calculated according to Equation 4.2

$$\text{Char yield } \% = [w_2/w_1]*100 \qquad \textbf{(4.2)}$$

where w_1 and w_2 are the weight of sample before and after ashing, respectively. The results show that the inorganic content of clay is remained as showing that the 5wt% of clay used to forming nanocomposites.

Table 4.3 : Ash contents and added clay percent

Samples	Ash (wt%)	Added Clay Content (wt%)
100PE	0	
80PE/15PE-co-MA/5I-44	2.6	5.1
80PE/15PE-g-MA/5I-44	2.7	5.2
80PE/15PE-co-MA/5I-30	3.3	5.6
80PE/15PE-g-MA/5I-30	2.9	5.1
85PE/10PE-co-MA/5I-44	2.7	5.2
85PE/10PE-co-MA/5I-30	3.3	5.7
90PE/5PE-co-MA/5I-44	2.5	4.8
90PE/5PE-co-MA/5I-30	2.7	4.6
100PP	0	
80PP/15PE-co-MA/5I-44	3.1	6.0
80PP/15PP-g-MA/5I-44	2.7	5.3
90PP/5PE-co-MA/5I-44	3.0	5.8
I-44 (inorganic content)	52	
I-30 (inorganic content)	58	

4.1.3 Mechanical testing

4.1.3.1 Tensile test results of nanocomposites

The polyolefin/clay nanocomposites were subjected to the tensile test and tensile strength, tensile modulus, yield strength, yield strain and strain at break were obtained from the 5 samples averaged. The results of the tensile test are given at Table 4.4. According to these values, modulus of PE/I-30 clay nanocomposites in PE nanocomposite samples had higher values as expected. This increment was also supported with the XRD measurement results (Table 4.1). Also, the mechanical properties enhanced by adding to the compatibilizer of PE-co-MA. This increasement is explained by the good dispersion of organoclay in polymer matrix. The comparison of the tensile test results were given in Figure 4.6, 4.7, 4.8, and 4.9.

Table 4.4 : Comparison of tensile test results

Samples	Tensile Strength (MPa)	Tensile Modulus (MPa)	Yield Strength (MPa)	Yield Strain (%)	Strain at Break (%)
100PE	10.6	225.0	8.1	5.6	450.0
90PE/5PEcoMA/5I44	10.4±0.4	289.2±17	7.9±0.6	4.7±0.4	21.9±3
90PE/5PEcoMA/5I30	10.5±0.4	322.1±99	8.3±0.6	4.7±0.8	41.4±5
85PE/10PEcoMA/5I44	9.7±0.3	332.1±77	7.4±0.5	4.3±0.6	20.3±10
85PE/10PEcoMA/5I30	10.2±0.4	321.0±53	8.0±0.8	4.6±0.7	30.6±5
80PE/15PEcoMA/5I44	9.9±0.1	390.9±129	7.7±0.1	4.1±0.7	17.9±7
80PE/15PEgMA/5I44	10.5±0.2	336.4±27	8.1±0.4	4.4±0.2	28.6±2
80PE/15PEcoMA/5I30	11.4±0.3	404.1±106	8.8±0.4	4.3±0.6	106.1±9
80PE/15PEgMA/5I30	11.3±0.3	356.8±25	8.3±0.4	4.3±0.7	115.2±7
100PP	31.8	1050.0	25.5	4.3	70.0
90PP/5PEcoMA/5I44	34.5±1.4	1559.9±289	31.3±1	4.1±0.4	11.6±3
80PP/15PEcoMA/5I44	26.6±1.3	1062.8±162	24.8±1	4.4±0.3	9.7±3
80PP/15PPgMA/5I44	37.1±1.1	1766.1±155	33.9±1	4.0±0.4	24.8±6

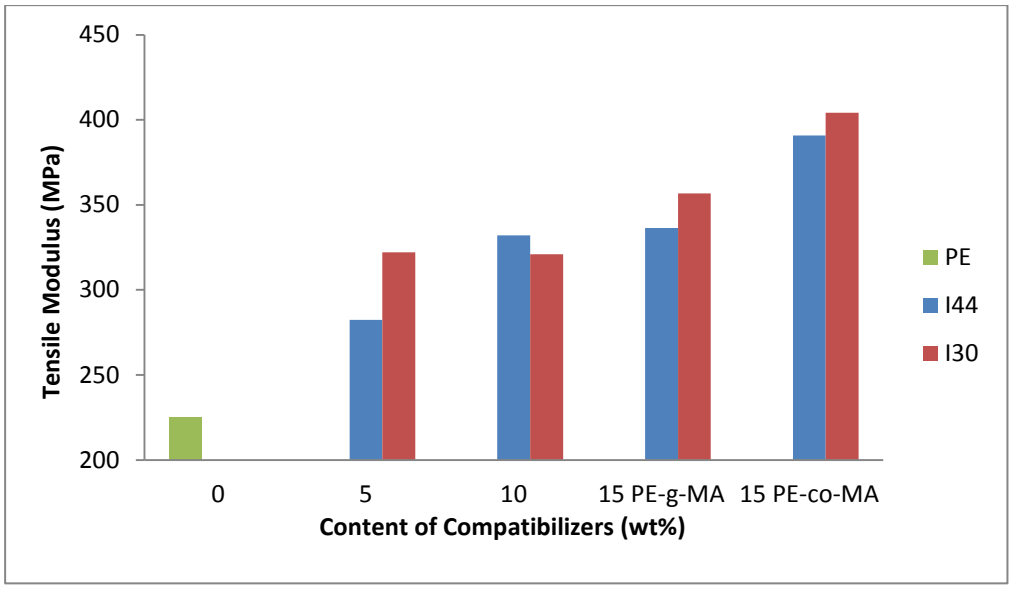

Figure 4.6 : Comparison of I-44 and I-30 for tensile modulus

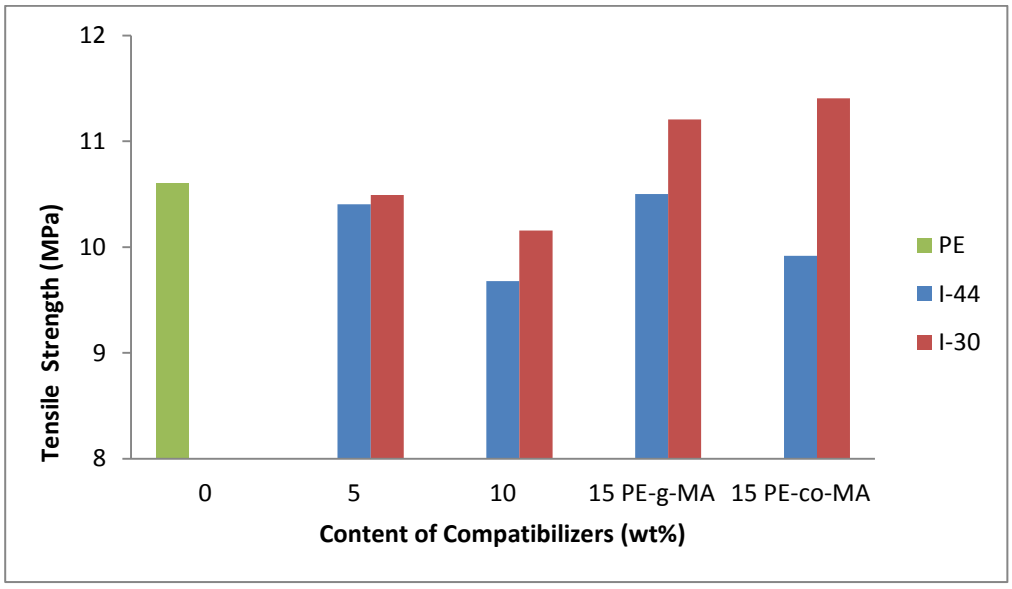

Figure 4.7 : Comparison of compatibilizers effect to impact strength

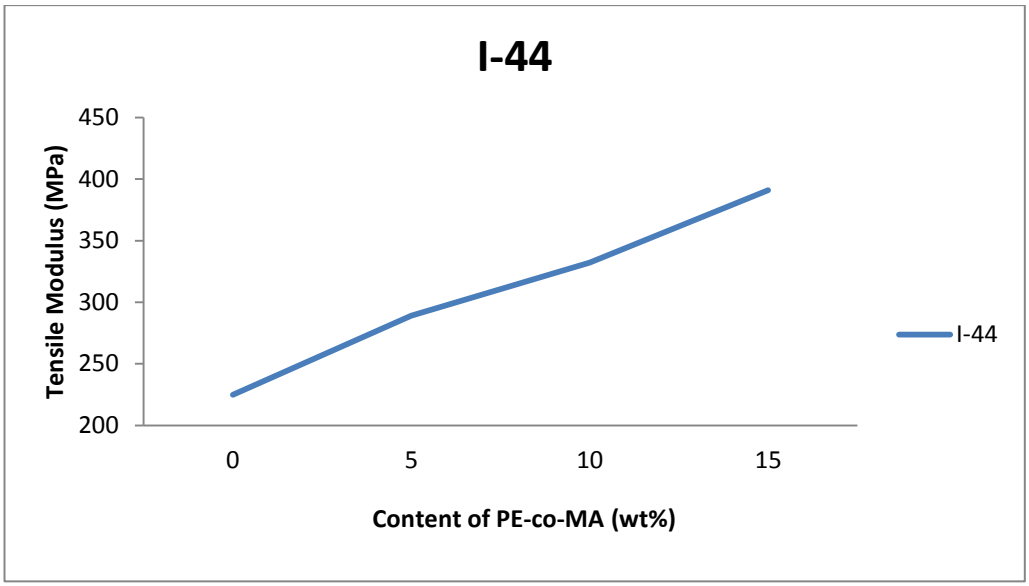

Figure 4.8 : Effects of PE-co-MA for tensile modulus of I-44

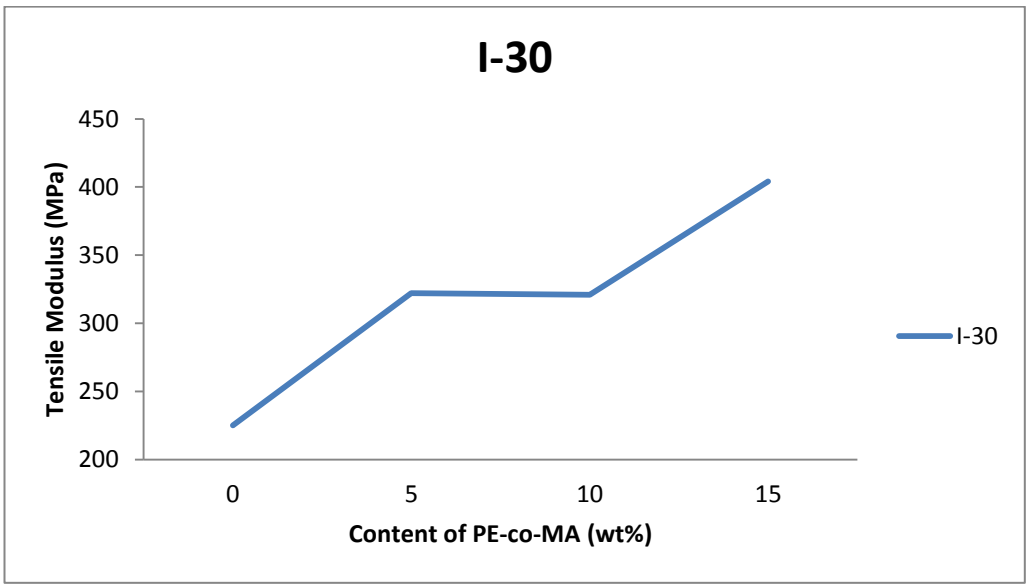

Figure 4.9 : Effects of PE-co-MA for tensile modulus of I-30

4.1.3.2 Izod impact test

Notched Izod impact tests were carried out for determination of impact strength of the nanocomposites.

The effect of compatibilizer was not observed more clear by adding 5wt% and 10wt% of compatibilizer, due to the weak dispersion between PE matrix and clay. However, the incorporation of 15wt% compatibilizer was increased the impact strength of PE/clay nanocomposites more than 80%. This results was also supported

with the XRD result. The comparison of the Izod impact test results were given in Table 4.5 and Figure 4.10, 4.11, 4.12, 4.13 and 4.14.

Table 4.5 : Test results of Izod impact strength measurements of samples

Samples	Impact Strength (Kj/m^2)
100PE	4.6
80PE/15PE-co-MA/5I-44	5.16±0.2
80PE/15PE-g-MA/5I-44	5.03±0.2
80PE/15PE-co-MA/5I-30	8.4±0.3
80PE/15PE-g-MA/5I-30	12.5±0.3
85PE/10PE-co-MA/5I-44	5.4±0.1
85PE/10PE-co-MA/5I-30	4.6±0.1
90PE/5PE-co-MA/5I-44	4.8±0.1
90PE/5PE-co-MA/5I-30	5.1±0.1
100PP	4.5
80PP/15PE-co-MA/5I-44	5.3±0.2
80PP/15PP-g-MA/5I-44	4.9±0.1
90PP/5 PE-co-MA/5 I-44	5.8±0.2

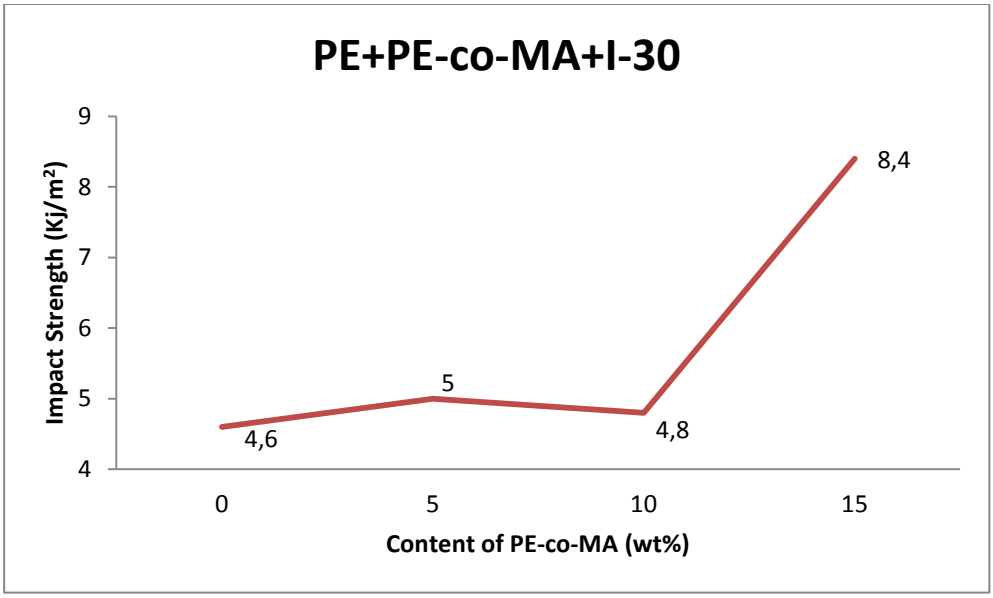

Figure 4.10 : Effects of the amounts of PE-co-MA compatibilizer for I-30

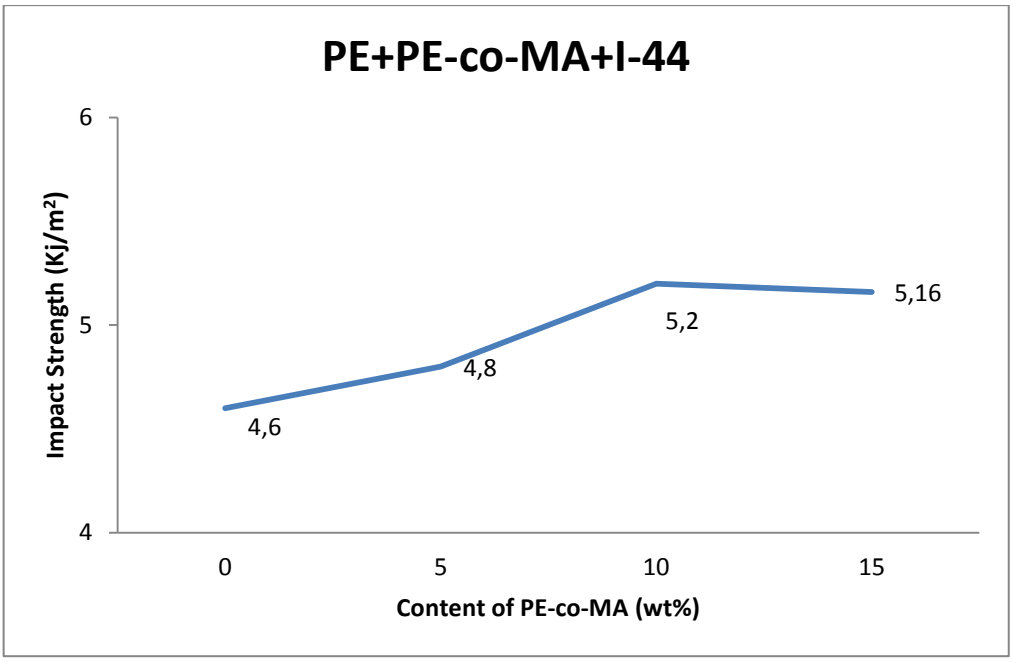

Figure 4.11 : Effects of the amounts of PE-co-MA compatibilizer for I-44

Adding of nanoclay has been found to improve to the impact strength of matrix. It is suggested that intercalated or exfoliated clay layers may help to hinder the crack caused by impact. The stress in the sample may be dispersed by intercalation of clay during the impact test, which posses higher strength that the matrix. Thus, it is observed that I-30 drastically improved to the impact strength of PE/clay nanocomposites than that of I-44. The I-44 clay was not be efficient on the impact strength properties of the PE/clay nanocomposites.

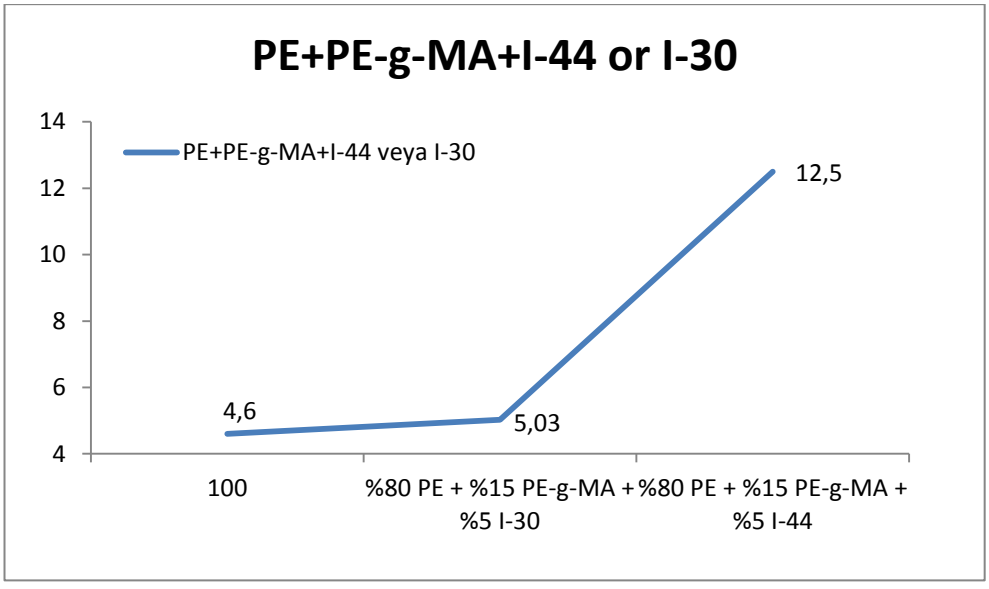

Figure 4.12 : Effects of different compatibilizers for impact strength

This results show that the addition of compatibilizer (PP-co-MA or PP-g-MA) increased the impact strength of PP.

It was observed that the highest impact strength was obtained by the addition of PP-co-MA at 15wt% content. The incorporation of PP-g-MA caused the slight improvement to the impact strength of PP/clay nanocomposites compared to the impact strength of PP. Besides, when the content of PP-co-MA is increased, impact strength of PP/clay nanocomposites changed from 5.3 to 5.8 Kj/m^2.

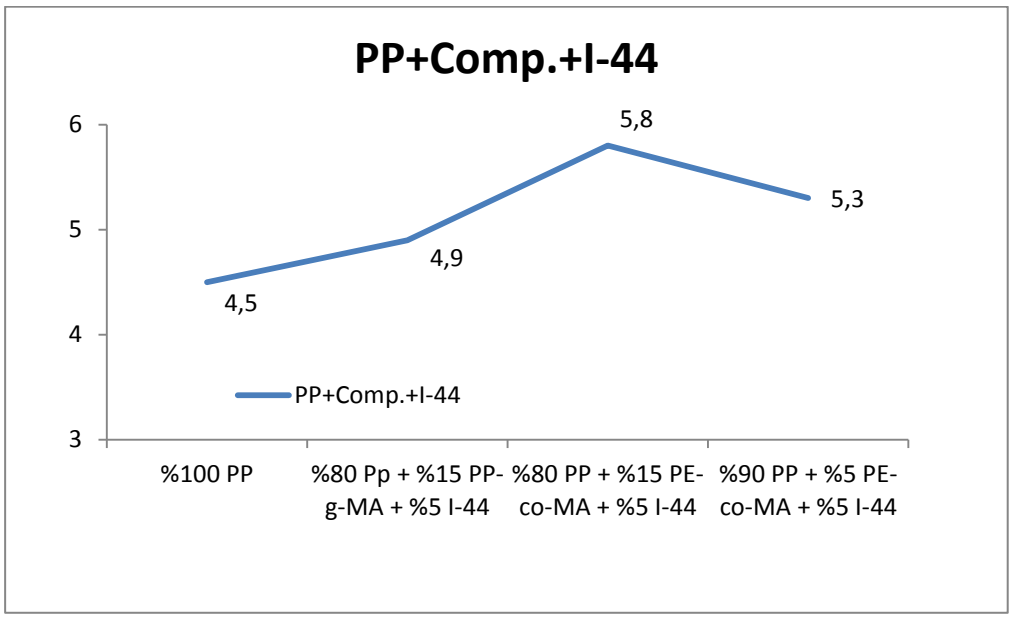

Figure 4.13 : Effects of different compatibilizers for impact strength

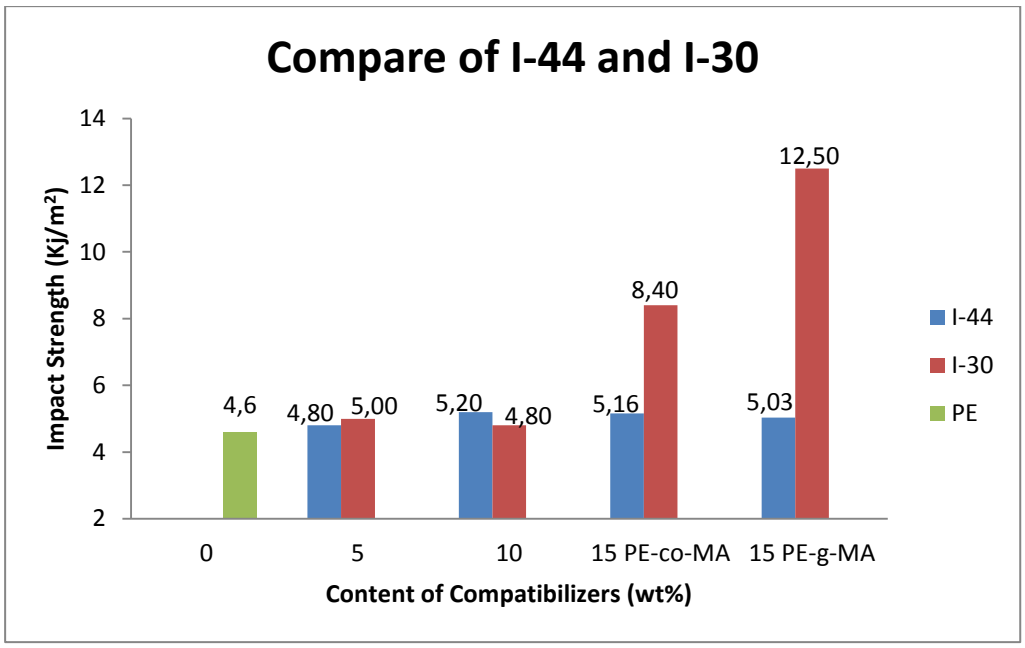

Figure 4.14 : Comparison of I-44 and I-30 for impact strength

4.1.3.3 Hardness

This results show that the tensile modulus values of the PE/clay nanocomposites have a significant increase, but the hardness values of these composites do not show an important variation. The hardness value of pure PE changes in between 52 and 55. Furthermore, the results of hardness values of composites obtained from Shore-D hardness test are given in Table 4.6 and Figure 4.15.

Table 4.6 : Test results of Shore-D hardness measurements of samples

Samples	Hardness (Shore-D)
100PE	52±1
80PE/15PE-co-MA/5I-44	55±1
80PE/15PE-g-MA/5I-44	54±1
80PE/15PE-co-MA/5I-30	55±1
80PE/15PE-g-MA/5I-30	55±1
85PE/10PE-co-MA/5I-44	54±1
85PE/10PE-co-MA/5I-30	52±1
90PE/5PE-co-MA/5I-44	49±1
90PE/5PE-co-MA/5I-30	52±1
100PP	74±1
80PP/15PE-co-MA/5I-44	73±1
80PP/15PP-g-MA/5I-44	78±1
90PP/5PE-co-MA/5I-44	74±1

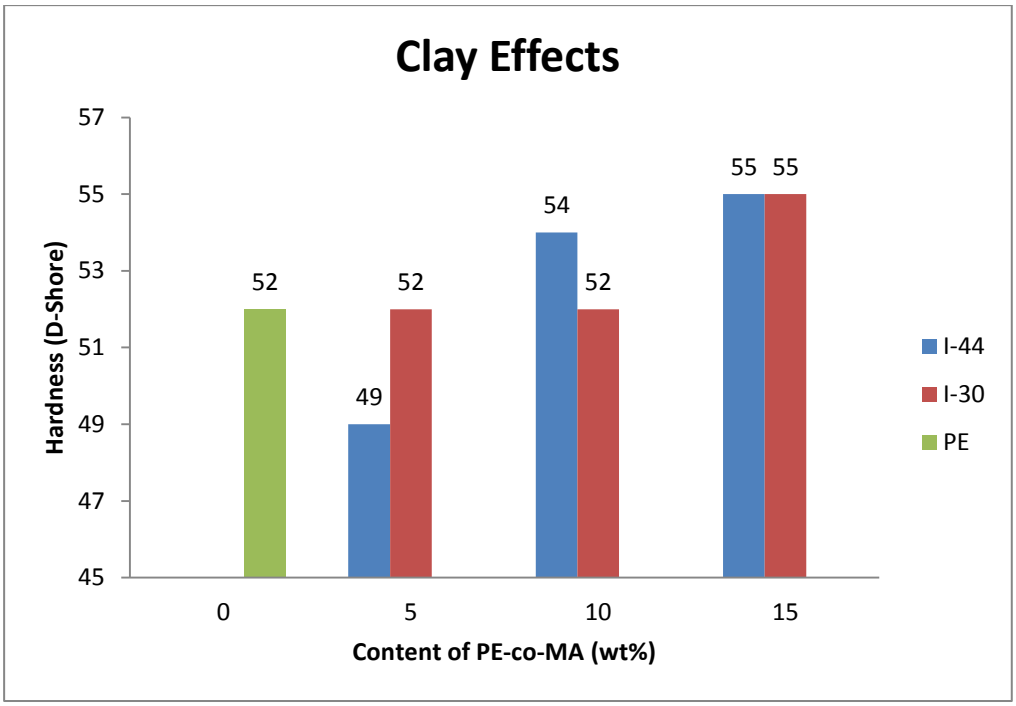

Figure 4.15 : Comparison of I-44 and I-30 for hardness

4.1.4 MFI

The influences to the processability of different types of compatibilizers with varying percentages to the polymer nanocomposites were observed by melt index measurements. The melt flow rate (MFR) of PE/clay and PP/clay polymer nanocomposites blends were measured as per ISO 1133 test standard. Table 4.7 shows the MFI values of nanocomposites and the comparison of the MFI results were given in Figure 4.16, 4.17 and 4.18.

In general, the MFI values of nanocomposites are lower than the MFI value of pure polyolefins which means higher melt viscosity. This shows that the effect of organoclay is more dominant than the effect of compatibilizer except for the nanocomposites with PE-co-MA with organoclays I-44. In the case of the content of the compatibilizers are increased, MFI values were also increased.

Table 4.7 : MFI values of nanocomposite samples

Samples	MFI (g/10min.)
100PE	23.5
80PE/15PE-co-MA/5I-44	27.1±0.9
80PE/15PE-g-MA/5I-44	12.5±0.5
80PE/15PE-co-MA/5I-30	22±0.8
80PE/15PE-g-MA/5I-30	8.4±0.3
85PE/10PE-co-MA/5I-44	24.3±0.8
85PE/10PE-co-MA/5I-30	23.5±0.7
90PE/5PE-co-MA/5I-44	22.2±0.8
90PE/5PE-co-MA/5I-30	21±0.7
100PP	29
80PP/15PE-co-MA/5I-44	11±0.5
80PP/15PP-g-MA/5I-44	8.9±0.3
90PP/5PE-co-MA/5I-44	5.1±0.2

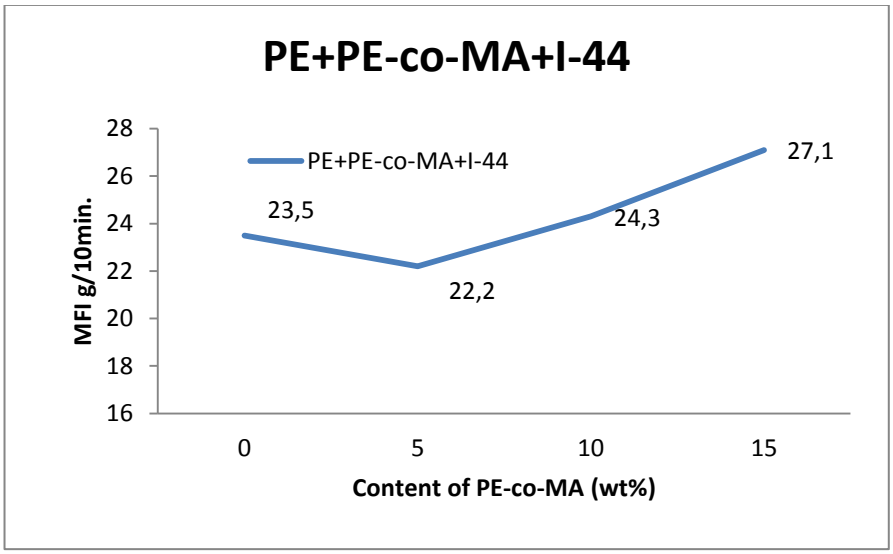

Figure 4.16 : Effects of different amounts of PE-co-MA compatibilizer for I-44

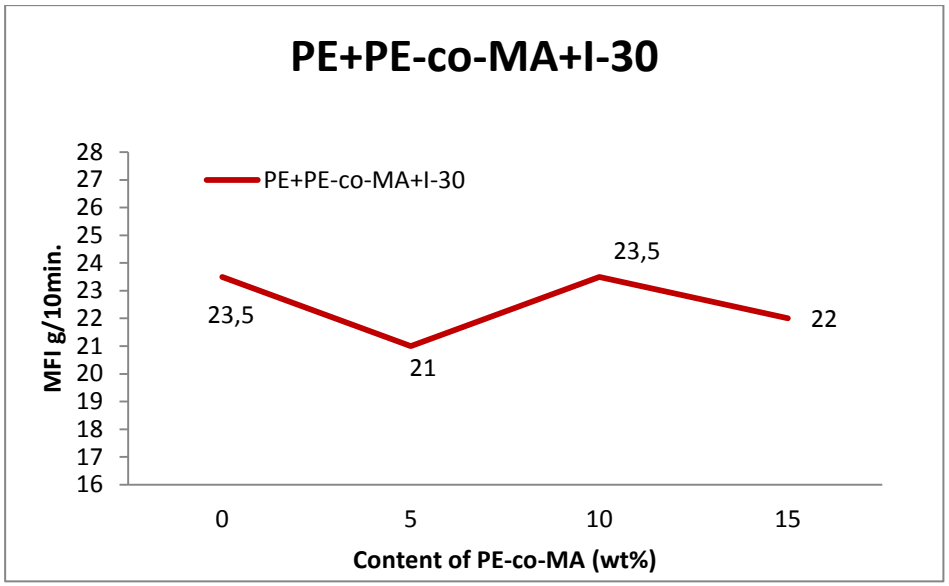

Figure 4.17 : Effects of different amounts of PE-co-MA compatibilizer for I-30

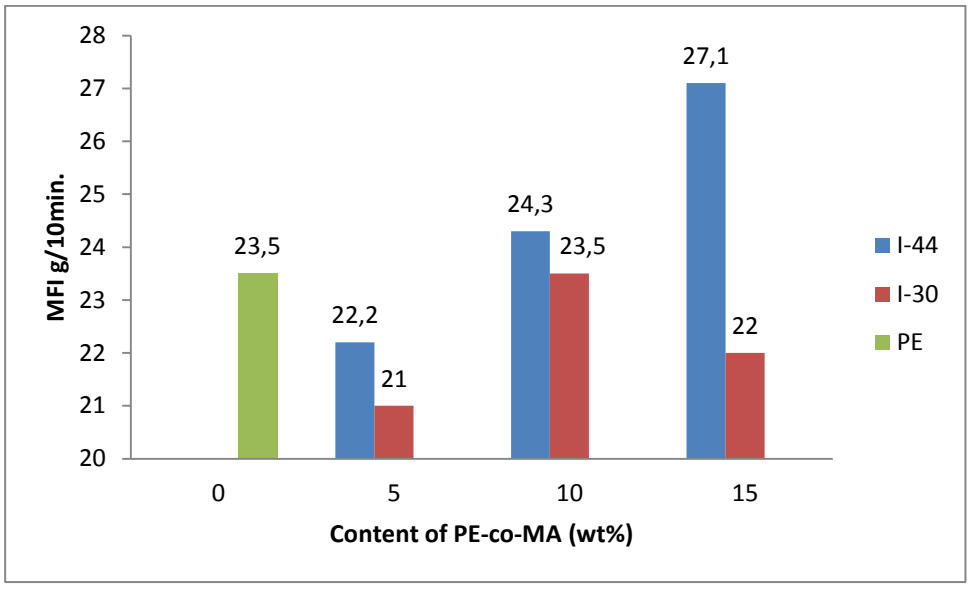

Figure 4.18 : Comparison of I-44 and I-30 for melt flow index

4.1.5 Density

The density values of additives and all samples was calculated by Radwag Was 220/X density kits. The results were shown in Table 4.8. The density value of PE was found 0.920 g/cm^3. On the other hand, clay adding increases the value to 0.940-0.960 g/cm^3. The results indicated that there were no significant differences for nanocomposites in the density values.

Table 4.8 : Density of the nano additives and the nanocomposite samples

Samples	Density (g/cm^3)
100PE	0.92
80PE/15PE-co-MA/5I-44	0.92
80PE/15PE-g-MA/5I-44	0.95
80PE/15PE-co-MA/5I-30	0.94
80PE/15PE-g-MA/5I-30	0.94
85PE/10PE-co-MA/5I-44	0.95
85PE/10PE-co-MA/5I-30	0.96
90PE/5PE-co-MA/5I-44	0.94
90PE/5PE-co-MA/5I-30	0.94
100PP	0.89
80PP/15PE-co-MA/5I-44	0.93
80PP/15PP-g-MA/5I-44	0.92
90PP/5PE-co-MA/5I-44	0.93

4.1.6 Glow wire test

Glow wire test (GWT) was done as per the procedure described in Section 3.4.6. GWT test results provide a way of comparing the ability of materials to extinguish flames and their ability to not produce particles capable of spreading fire. Glow wire test results showed that all samples achieved the test at temperature of 550°C and 650°C. All the nanocomposites passed the GWT successfully.

5. CONCLUSION

Polymer nanocomposite (PNC) samples containing PE and PP polyolefins were prepared by melt compounding method in order to improve the mechanical properties of polyolefins. The samples were prepared by using different types of polyolefins and the different types and percent of compatibilizer with two types of organoclay.

All the PNC samples were prepared in twin screw extruder at between 170^{o}C and 210^{o}C mixing temperature and 350 rpm screw speed. PE-co-MA compatibilizer were used at amount of three different loading levels (5wt%, 10wt% and 15wt%). PE-g-MA compatibilizer were used as 15wt% content. The content of organoclays was kept constant as 5wt% in all samples.

The prepared 13 samples were investigated structurally by XRD, thermally by DSC, mechanically by universal testing machine, Izod impact test machine, and hardness test device. The processability of samples were determined by using MFI measurements.

The distances between clay layers (d_{001}) of the samples showed better results in 15wt% compatibilizers loaded samples in previous studies and our experiments as well. 80PE/15PE-co-MA/5I-30 and 80PE/15PE-g-MA/5I-30 samples showed better results than those of the nanoclay I-44 containing samples. Interactions between organoclay and polymer were improved as a consequence of higher affinity and hydrogen bonding between the maleic anhydride group and the modified clay surfaces as well as the chemical compatibility between the polyethylene matrix and polyethylene in the compatibilizer structure.

Mechanical properties of the polymer nanocomposite samples were investigated and the same tendencies were found in tensile strength and tensile modulus values. Tensile strength and tensile modulus values of the samples 80PE/15PE-co-MA/5I-30 and 80PE/15PE-g-MA/5I-30 showed the best results. The measured mechanical

properties of PNCs showed a regular increase with an increasing compatibilizer content, although 5wt% compatibilizer addition was not very effective for the systems. Addition of PE-co-MA as a compatibilizer was more effective than PE-g-MA. The dispersive forces were more efficient than the cohesive forces between the clay platelets for all nanoclay types due to the ratio between organoclay and compatiblizers. The tensile modulus values of the PE/clay nanocomposites have a significant increase, but the Shore-D hardness values of these nanocomposites do not show an important variation. Finally, the best improvement in mechanical properties were obtained by the PE/organoclay nanocomposites containing 15 wt% PE-co-MA and 5 wt% I-30 with %79.6 increase in tensile modulus.

The impact strengths of PE/organoclay nanocomposites were also increased more than 80% as a result of adding of 15wt% PE-g-MA.

Due to the nucleating ability of organoclays and hence the increased crystallinity, tensile properties were also improved to a small extent. This results are supported with DSC measurements. MFI value results showed that when the amount of compatibilizer is increased, the MFI values were increased as well. It was found that there were no significant differences in the density values of the nanocomposites.

3 nanocomposite samples were prepared by using I-44 organoclay in PP matrix. Two kinds of compatibilizer were used to compare their effects on the properties of these PNC samples. From DSC analysis, the crystallinity of PP nanocomposites were increased 55%. Also, the mechanical properties showed that the incorporation of 15 wt% PP-g-MA with 5 wt% I-44 was increased in the tensile modulus of PP/clay nanocomposites but the hardness values of these composites do not show an important variation. The incorporation of PP-g-MA caused the slight improvement to the impact strength of PP/organoclay nanocomposites compared to the impact strength of PP. When addition of compatibilizer and clay were added into the PP matrix, it was observed that the MFI values of nanocomposites were decreased. It was found that there were no significant differences in the density values of PP/clay nanocomposites. From the results of the measurements, PP-g-MA was found to be a more effective compatibilizer than PE-co-MA for this system.

Glow wire test results showed that all PE & PP nanocomposite samples achieved the test at temperature of 550°C and 650°C.

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